CONTENTS

OBSERVATIONS ON THE PERMEABILITY OF HYGROSCOPIC MATERIALS TO WATER VAPOUR

I. OBSERVATIONS AT RELATIVE HUMIDITIES LESS THAN 75%[1]

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Abstract

It is pointed out that experimental work has shown that for the transpiration of moisture through hygroscopic materials two distinct regions of relative humidity can be distinguished: (i) A region below some value between 70 and 80% where the moisture movement is proportional to the vapour pressure difference, and (ii) a region of high relative humidity where the moisture movement is not directly proportional to the vapour pressure. A theory is advanced that these two regions correspond to the two conditions in which water may be present in a hygroscopic material: (i) the water may be molecularly adsorbed, that is to say, the water is bound by the affinity of the molecules of water for those of the solid on which it is adsorbed; (ii) the water may be held in small fissures in the sub-microscopic structure of the sorbing material by capillary forces. The mechanism by which the moisture will move through the material would be different in the two cases and would result in the distinction between regions of high and of low relative humidity.

A short discussion is given of Fick's law showing the form in which it might be expected to apply in the two cases. Measurements are given for fibreboards showing that below 75% relative humidity the resistance of the board to moisture transpiration is proportional to the thickness. The moisture content gradients through fibreboard samples have been determined. The diffusance through a board in which the moisture content gradient is opposed to the vapour pressure gradient shows that the latter is the important factor, and the determination of the moisture content gradient indicates that at these low humidities Fick's law is applicable.

Introduction

The emphasis which, during recent years, has been placed by the building trade on the prevention of the condensation of moisture in the walls and roofs of buildings has led to a study of the movement of water vapour through these structures. The treatment of this problem by the use of diffusion coefficients has been outlined (3, 5, 14). In these discussions the assumption was made that the movement of water vapour obeyed Fick's law and that, on such an assumption, the vapour gradients through any structure could be calculated in a manner similar to that used to obtain temperature gradients. It was pointed out that the assumption that the movement of water vapour was a pure diffusion obeying Fick's law was not an accurate statement, since

in the case of hygroscopic materials it is well known that there is a much more intimate relation between the water molecules and the material than would hold in the case of pure diffusion.   The assumption, however, was justified on the basis that any errors introduced in this way would be negligible compared to those that occur when it is attempted to apply diffusion coefficients measured on a small scale in a laboratory to a structure such as a house, where the carpenter or contractor has little knowledge of the mechanism of moisture condensation and acts accordingly.

Rowley (12) considers that the transmission of moisture through hygroscopic materials "will be by capillarity or some similar process and will not depend upon vapour pressure difference".   He assumes that the movement of moisture in a hygroscopic material is a function of the moisture content gradients.   Since the moisture content of a hygroscopic material depends on the relative humidity and not on the absolute vapour pressure, it follows that the moisture movement depends primarily on the former and only indirectly on the latter.   Rowley shows that with these assumptions it is possible to have vapour movement through a wall "from the side in contact with the low vapour pressure air to that in contact with the high vapour pressure air".

The difference between the two conceptions, in one of which the vapour pressure is the driving force and in the other the moisture content, is so fundamental to any theory of moisture transfer that it is essential that the position be clarified at the earliest possible moment.   A study of the published work on this subject establishes the fact that this difficulty, while not precisely stated, has been apparent to virtually all workers in the field.   As stated by Carson (9), the position would seem to be that for all humidities less than 70 to 80%, the rate of transpiration of moisture is proportional to the difference in vapour pressure.   For higher humidities a linear relation between the rate of moisture transfer and vapour pressure difference does not exist.

The work on which this conclusion is based is varied and taken from several sources.   Some interesting work of Edwards and Wray (11) is quoted in which the vapour pressure difference was kept constant while the temperature, and in consequence the relative humidity, was varied over a considerable range.   The rate of transpiration of moisture remained virtually constant, irrespective of temperature, until the relative humidity on one face exceeded about 70%, whereupon the rate of transpiration began to increase (even though the temperature was decreasing).   This work was done on paint films, but Taylor, Herrmann, and Kemp (13) arrived at the same conclusion in their experiments on rubber, and Church and Scroggie (10) in some tests made on cellophane.   Abrams and Brabender (1) conclude that "the water vapour permeability is directly proportional to the actual water vapour pressure differential across the two faces of the sheet", and state further that "the difficulty in obtaining evidence to support such a statement lies in the establishment of definite relative humidities directly at the two opposite faces of the sheet".   On the other hand, Brabender (8) finds later that "the rate of transpiration of water vapour through a sheet has been observed to depend

not only on the vapour pressure gradient across the two faces of the sheet but also on the range of humidities chosen for the test". The tests on which this observation is based were made in the first case with 0 and 50% relative humidity on the two sides of the sample, and in the second case with 50 and 95%. He sums up his experimental results as follows: "The average permeability with a vapour pressure gradient of 9.37 mm. of Hg (i.e., with 0% and 50% R.H.) was about 0.27 gms. per sq. m. per 24 hours, as compared to 11.12 gms. at 8.44 mm. Hg under the higher humidity conditions (i.e., 50% and 95% R.H.)".

All the experimental work, therefore, tends to point to the fact that as far as the transpiration of moisture is concerned there are two distinct regions: (i) below some value of relative humidity between 70 and 80%, a region where the moisture movement is proportional to vapour pressure difference, and (ii) a region of high relative humidity where the moisture movement is not directly proportional to the vapour pressure. This difference in the behaviour of hygroscopic materials at high and at low relative humidities immediately suggests that there is a distinct difference between the mechanism of the moisture movement in the two cases. The magnitude of the difference found by Brabender is such as to suggest that this is a difference in kind rather than degree. The nature of the water present within the hygroscopic material must be different in the two cases. Recent work on moisture in wood suggests a possible explanation. Thus Barkas (6) makes a sharp distinction between (i) molecular sorption where the water is bound by the affinity existing between the molecules of water and those of the solid on which it is adsorbed, and (ii) capillary sorption where liquid water is present in the interstices of the solid and where the formation of a meniscus results in a vapour pressure lower than saturation. Barkas is even able to distinguish experimentally between these two types of sorption, and his work indicates that, were no capillary absorption present, the saturation moisture content of wood would be around 23%. It is obvious, however, that the two types of sorption will overlap and that capillary sorption will be going on when the moisture content is much less than 23%. The minimum vapour pressure at which capillary sorption can take place depends on the radius of the smallest interstice where the liquid may condense according to laws governing the vapour pressure over a curved meniscus. An investigation (7) on the relationship between volume-shrinkage and moisture content indicates that below 6% moisture content there is no capillary sorption, and that a linear relation is obtained between shrinkage and moisture content up to about 16% moisture content, indicating that below this the capillary sorption has not been large enough to influence the measurements. Above 16% the curve bends sharply, showing the influence of capillary sorption.

A theory such as this accounts very nicely for the observations on the rate of moisture transpiration. It has already been suggested by Edwards and Wray (11) as an explanation for the diffusion in the case of paint films. Below 80% relative humidity the greater part of the sorbed moisture is mole-

cularly sorbed and might well be expected to move through the material under the influence of vapour pressure. That the vapour pressure isothermal for most hygroscopic materials is relatively straight within this region would support this hypothesis. Above 80% relative humidity the amount of water retained by capillary attraction begins to be appreciable. That such water is not dependent on the vapour pressure is immediately evident from the fact that the vapour pressure isothermals are steeply curved in this region. Water present within a material in this condition would hardly obey a simple linear vapour pressure relation. Probably in this case the moisture content gradient is the predominant factor but more experiments will be needed before this can be accurately known.

The presence of these two regions in which the transpiration of moisture obeys different laws is of extreme importance both for measurements of the permeability of materials and also for their practical use. In particular, it means that materials tested at high humidities cannot be directly compared with those tested at humidities lower than 80%. Naturally, any test method must simulate as closely as possible the practical conditions under which the material will be used. In the case of building materials installed as vapour barriers in walls the relative humidity will, in general, be within the lower range so that a test method using a relative humidity of 75% will be appropriate. Thus the diffusances obtained by the method outlined previously (5) can be directly applied to walls as suggested in that paper. In the case where the humidities are above 80% the simple theory that follows from Fick's law would not be applicable, and at present there is no simple method of computing the rate of vapour transpiration. It is important to realize, however, that test methods employing saturated or nearly saturated atmospheres may give permeabilities vastly different from those obtained with low humidities.*

In this paper a study will be made of the transmission of water vapour through hygroscopic materials at relative humidities below 75% in order to discover whether deviations from Fick's law are of sufficient magnitude to vitiate the conclusions derived by the use of such a law. For example, if, as Rowley has suggested, it were possible to have "vapour movement through a wall from the side in contact with the low vapour pressure air to that in contact with the high vapour pressure air" then Fick's law as ordinarily stated, giving diffusion proportional to pressure gradient, would obviously not be applicable. Since the general opinion seems to be that at relative humidities lower than 80% the rate of vapour transpiration is proportional to the pressure gradient, there would seem to be no reason why Fick's law should not be used to calculate moisture conditions within a wall as outlined in (5). It is the intention here, first to study Fick's law in order to ascertain exactly what implications are involved and, second, to describe experiments

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* It seems probable that with many hygroscopic materials there is no increase of permeability at high humidities. The size of the pores within the material would seem to be the critical factor and with pores either smaller or larger than a certain critical range the contribution to the permeability made by capillary movement would be negligible.

in which these implications are tested.   It is hoped that the investigation will be continued so as to cover higher humidity conditions.

Implications of Fick's Law

In order to ascertain what is implied by the treatment of water vapour transpiration by Fick's law, it is instructive to write the law in its differential form, thus:

$$\frac{dc}{dt} = D_p \frac{\partial^2 P}{\partial x^2} \tag{1}$$

where c is the concentration and P the pressure of the gas at time t in a plane at a distance x from the origin measured in the direction of diffusion. D_p is the diffusion coefficient.

In some cases the law is written in the form

$$\frac{dc}{dt} = D_c \frac{\partial^2 c}{\partial x^2} . \tag{2}$$

Equations (1) and (2) are identical when, and only when, the concentration is directly proportional to the pressure, i.e., when the diffusing gas obeys Henry's law.   In the case of water vapour diffusing through a hygroscopic material it is obvious that this is not true.   The concentration of water vapour in such a material is dependent on the relative humidity and is only indirectly related to vapour pressure; moreover, the relation between relative humidity and moisture content is very complex, and it is only over a very small portion of the humidity range that it is even approximately linear. The relation is further complicated by the hysteresis effect.   There is, then, no grounds on which Equations (1) and (2) can be considered identical in the case of water vapour diffusing through hygroscopic materials.   On the contrary they represent the two points of view outlined in the preceding section. In Equation (1) the vapour pressure is the driving force behind the transpiration of moisture, while in Equation (2) the moisture content plays this role.

By integration from Equation (1) we obtain the diffusion equation in the form in which it is generally applied:—

$$W = D_p At \frac{dP}{dx} \tag{3}$$

where W is the weight of gas diffusing through an area A in time t when the pressure gradient is $\frac{dP}{dx}$.   Similarly, if we had started from Equation (2) we should have obtained

$$W = D_c At \frac{dc}{dx} . \tag{4}$$

Now the equations in this form can be directly checked for it is easy to plan experiments in which the results to be expected in the two cases are different. In the extreme case, by a suitable adjustment of humidity and temperature conditions, it is possible to perform an experiment in which $\frac{dP}{dx}$ and $\frac{dc}{dx}$ have the opposite signs, and thus the sign of W will indicate immediately the equation that is applicable.
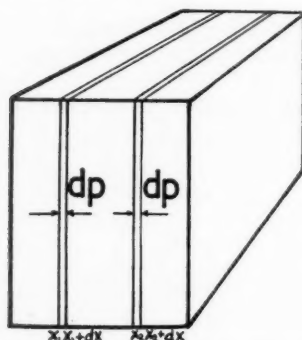
FIG. 1.   *Diffusion of gas through an infinite sheet of material.*

There is another consideration that is perhaps worth elaborating.   Consider a block of material such as shown in Fig. 1 through which a gas is diffusing from left to right and in which equilibrium conditions are established.   If there is no transfer of gas in the $y - z$ plane then the amount diffusing across unit area in x_1 must be equal to that diffusing across unit area in x_2.   If this were not true there would be an increase or decrease in the concentration of the gas at some point between x_1 and x_2 which would be contrary to the assumption of equilibrium.   If we assume that the diffusion coefficient D_p is a constant for the small changes of pressure involved, then

$$\left(\frac{dP}{dx}\right)_{x_1} = \left(\frac{dP}{dx}\right)_{x_2}.$$

In other words, if the equation holds, the gradient must be constant throughout the material and the relation between P and x must be linear.   Similarly, if Equation (4) applied then

$$\left(\frac{dc}{dx}\right)_{x_1} = \left(\frac{dc}{dx}\right)_{x_2}$$

and c is a linear function of x.   These considerations again emphasize the incompatibility of the two equations in those cases where there is no direct proportionality between moisture content and pressure.

Since it has been shown that there must be a linear relation between P and x or c and x, as the case may be, it follows that W must be inversely proportional to the thickness of the material.   Thus a determination of the variation in W with thickness will show whether an equation of the general form (3) or (4) is applicable.   An investigation of this nature, however, is not capable of distinguishing between the two equations given above.

Variation of Resistance with Thickness

As the first step in determining the theory underlying the movement of water vapour through materials, it is interesting to determine the relation between diffusance and thickness.   Some preliminary results on this subject have been already published (5), and here this work will be extended to

TABLE I

WOOD

Sample	Thickness, cm.	Diffusivity, gm./24 hr./sq. metre/$\frac{\text{mm. Hg.}}{\text{cm.}}$	Diffusance, gm./24 hr./sq. metre/mm. Hg.	Resistance
Wood I	4.378	2.405	0.549	1.821
Wood II	4.290	2.658	0.620	1.61
	3.192	2.366	0.741	1.35
	2.135	2.080	0.974	1.03
	1.093	1.649	1.51	0.662
	0.459	1.597	3.48	0.287
Wood III	4.329	2.255	0.521	1.92
	3.016	2.096	0.695	1.44
	2.055	1.710	0.832	1.20
	1.159	1.553	1.34	0.746
Wood IV	4.329	1.286	0.297	3.37
	3.259	1.835	0.563	1.78
	2.141	1.783	0.833	1.20
	1.296	1.569	1.21	0.826
Wood V	1.43	1.62	1.13	0.885
	1.22	1.60	1.31	0.763
	1.03	1.32	1.28	0.781
	0.82	1.31	1.60	0.625
	0.59	1.39	2.35	0.426
	0.41	1.37	3.36	0.298
Wood VI	2.03	1.25	0.61	1.639
	1.64	1.34	0.82	1.220
	1.26	1.41	1.12	0.893
	0.80	1.43	1.80	0.556
	0.43	1.34	3.13	0.319

greater thicknesses. The results of the measurements are given in Tables I and II, and are shown graphically in Figs. 2 and 3. In the figures the resistance, which is equal to the reciprocal of the diffusance, is plotted against the thickness. The same sample was used throughout one series of measurements—the diffusance being determined first at the greatest thickness and then at lesser thicknesses as the sample was reduced by sanding. For these measurements the samples were mounted in a crystallizing dish as previously described (5) with anhydrous calcium chloride within the cell and an atmosphere of 75% relative humidity outside.

The results already published for wood (5) have been included with the present measurements. From a study of Fig. 2 it is apparent that when the measurements on wood are extended from a thickness of 1 to 2 in., the agreement is not nearly as good, but that there is considerable scatter in the results. There seems to be a definite divergence as the thickness is increased. These measurements were all made with the moisture moving transversely to the grain, but no precautions were taken to distinguish between flow radial and

TABLE II

Fibreboard

Sample	Thickness, cm.	Diffusivity, gm./24 hr./sq. metre/$\frac{\text{mm.Hg.}}{\text{cm.}}$	Diffusance, gm./24 hr./sq. metre/mm. Hg.	Resistance
Fibreboard I	5.224	44.1	8.44	0.119
	4.039	42.0	10.4	0.096
	2.614	36.3	13.9	0.072
	1.501	32.1	21.3	0.047
	0.955	32.6	34.1	0.036
Fibreboard II	5.232	45.7	8.7	0.114
	4.018	44.4	11.1	0.091
	2.378	38.4	16.1	0.062
	1.241	39.2	31.6	0.032
Fibreboard III	5.306	46.7	8.80	0.114
	4.137	45.3	11.0	0.091
	3.107	45.5	14.7	0.068
	2.035	41.4	20.4	0.049
	1.083	34.3	31.6	0.032
	0.594	27.9	47.0	0.021
Fibreboard IV	4.981	70.5	14.2	0.071
	3.753	67.2	17.9	0.056
	3.048	67.7	22.2	0.045
	2.014	58.8	29.2	0.034
	0.862	42.2	48.9	0.020

tangential to the annual rings. The results would seem to indicate that variations in the structure of the wood have a very appreciable effect on the amount of vapour transmitted. A striking example of this is furnished by Sample IV in Table I. The original sample (thickness, 4.329 cm.) had a resistance of 3.37, which is about twice as great as that of the other samples of comparable thickness. When the thickness was reduced to 3.259 cm. the resistance dropped to 1.78, in good agreement with the general run of results. Why had the original sample such a high resistance? An examination of the sample in question suggested an explanation. A cross-section of it is shown in Fig. 4, the general shape of the annual rings being indicated. In the original sample the water vapour could not pass from one surface to the other without diffusing through at least one annual ring. When, however, the thickness was reduced by cutting off the top centimetre as indicated by the dotted line, the vapour could get from one surface to the other without necessarily crossing any annual ring. If the resistance of the dark portions of the rings was much greater than that of the light, a large difference would be expected between the resistances of the two samples indicated in the diagram.

It is evident then, that wood is not good material with which to carry out experiments of this nature, since the resistance to moisture movement is not constant through the sample. For this reason the experiments were con-

tinued using fibreboard instead. Fibreboard is, like wood, a cellulosic material, being composed of wood fibres, but it differs from wood in that it is, at least from a macroscopic point of view, homogeneous.   There is evidence (2, 4) that the fibres in the surface layers have a greater degree of orientation than those
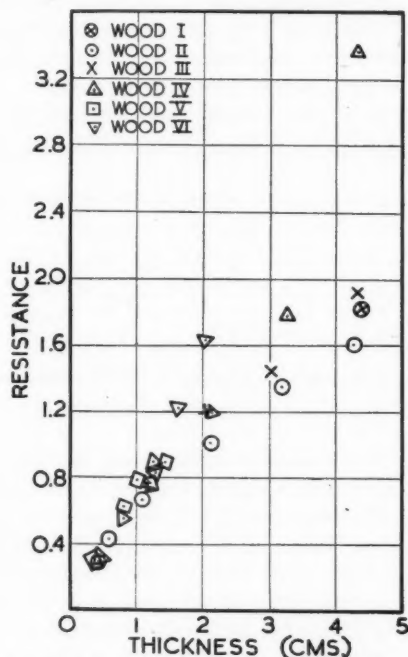

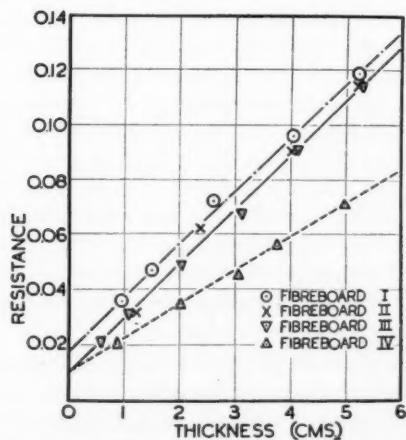FIG. 2.   *Variation of resistance with thickness of wood.*

FIG. 3.   *Variation of resistance with thickness of fibreboard.*

in the body of the material, but the effect of this on moisture flow should be small and, if necessary, can be eliminated by removing the surface layers.

The results obtained with fibreboard samples are given in Table II and are represented graphically in Fig. 3, study of which shows that the relation between resistance and thickness can be nicely represented by a straight line. The lines for Fibreboards I, II, and III are roughly parallel and differ only slightly with respect to the intercept on the Y-axis. The line representing Fibreboard IV has a slope different from that of the other three; this is easily explained by the fact that it was taken from a different piece of fibreboard.
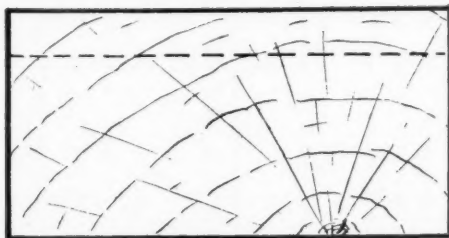

FIG. 4.   *Wood sample showing how the annual rings may influence the moisture transfer.*

According to Fick's law the curve representing resistance against thickness should pass through the origin to signify that with zero thickness there should be infinite diffusion. The fact that with these fibreboard samples there would still be a small residual resistance, even when no fibreboard is present, implies that the air between the desiccant and the lower surface of the sample has an appreciable resistance. Another way of looking at this is to consider that the actual vapour pressure drop from the air in contact with the lower surface of the sample to that in contact with the upper surface is less than the total vapour pressure difference between the desiccant and the external atmosphere by a small amount corresponding to the pressure drop that is necessary for diffusion up to and from the surfaces. The actual value of this residual resistance as determined from the curves is about 0.01. This has a quite appreciable effect on the measured diffusance of samples of low resistance. Thus the changes in the diffusivity of the samples in Table II as the thickness is decreased is a result of this. The effect, however, decreases with increasing resistance. Thus for the case of a material, such as wood, where the resistance of a specimen 1 cm. thick is about 0.7, the error introduced by a residual resistance of 0.01 is only between 1 and 2%. For all samples having a diffusance less than 1.0 gm. per 24 hr. per sq. metre per mm. of mercury the error introduced by this resistance would be less than 1% and can be neglected in the testing of such materials.

Another possible explanation of the residual resistance is that the calcium chloride does not reduce the relative humidity within the cell to a value that is essentially zero. If a small residual pressure existed within the cell the effect would be the same as if there was an additional resistance as described

above. According to the International Critical Tables (vol. 3, p. 385) air dried with granulated calcium chloride has a residual vapour content of from 0.14 to 0.25 mg. of water vapour per litre. At 90° F. this represents less than $\frac{1}{2}$ of 1% relative humidity. Air dried with sulphuric acid has a vapour content of 0.003 mg. per litre, equivalent to about 1/100 of 1% relative humidity. Thus for our work both materials should be satisfactory. However, in order to ascertain if the use of calcium chloride rather than some more efficient desiccating agent was affecting the results, a specimen of building paper was tested with both calcium chloride and concentrated sulphuric acid. The results were: 0.111 gm. per 24 hr. per sq. metre per mm. of mercury with the former and 0.116 with the latter. This indicates that calcium chloride is a sufficiently good desiccator in tests of this nature.

One point has become apparent, however, from these tests—care must be taken that the calcium chloride does not absorb sufficient vapour to become moist, in which case the residual pressure will rise. In some tests the quantity of water diffusing through the sample per unit time decreased slowly after a certain amount of water had been absorbed; this indicated a rise in residual pressure. For this reason, in all tests care is taken that the amount of water absorbed by the calcium chloride never exceeds 4 or 5 gm.

The work described above would indicate that a linear equation can be reliably used to calculate the amount of diffusion through any thickness of material if allowance is made for the residual resistance. Some doubt, however, might still arise as to whether it is permissible to use such a relation to compute the combined resistance of two separate samples. As a check on this, the diffusances of two different building papers were determined and the two samples were then placed in one cell, one over the other, and the diffusance through the combination was measured. The results are given in Table III.

TABLE III

	D	$R = \dfrac{1}{D}$
Paper A	4.20	0.238
Paper B	4.17	0.240
$A + B$	2.18	0.459

The resistance of the combination $A + B$, obtained by adding the individual resistances, is 0.478. This is equivalent to a diffusance of 2.09. The difference between this and the measured value is so small that it can be concluded that no error would be caused by the use of Fick's law in such cases.

The Moisture Content Gradient

It was pointed out in the beginning of this paper that, according to the form in which Fick's law is used, either the moisture content gradient or the vapour pressure gradient must be constant through a sample. It is interesting,

therefore, to determine the moisture content at various positions in a sample
when equilibrium conditions have become established. The instruments
available for the measurement of moisture content are not sufficiently accurate
or sensitive for a determination of the moisture content gradient in situ, but
the exchange of moisture between sample and atmosphere is sufficiently slow
to allow a sample to be removed from the cell, cut up into small sections
parallel to the faces, and weighed. The difference in weight between the
sections of the samples when first cut up and when dried represents the amount
of moisture absorbed by that section and can easily be expressed as a per-
centage by weight. The thickness of the sections can be measured and it is
then possible to plot the change in moisture content from the surface in contact
with the external air to that next to the desiccant.

This work was, for the greater part, carried out on fibreboard samples 2 in.
thick. These were waxed in a glass crystallizing dish, placed in the humidity
chamber, and the moisture diffusion was determined. The sample was then
quickly removed, cut up, weighed, and the moisture content calculated. There
was, of course, a slight exchange of moisture between the sample and the
atmosphere from the time it was removed from the humidity chamber until
it was placed in the weighing bottles for weighing. The effect of this, however,
is not great.
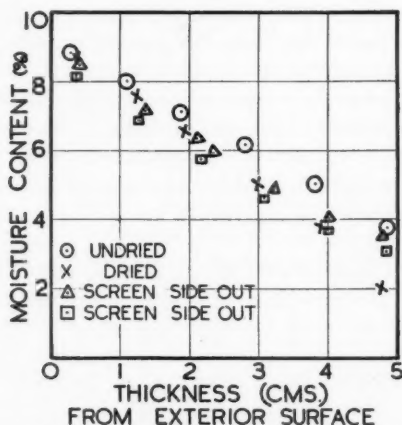
FIG. 5.   *Moisture content gradients through fibreboard samples.*

The results from some of these experiments are given in Figs. 5 and 6.
The curves obtained from fibreboard samples such as these depend to some
extent on the initial condition of the sample. Because of the hysteresis in
the moisture regain curve it is obvious that the moisture content at any relative
humidity will be greater if equilibrium in the fibreboard is approached from
a higher relative humidity than if it is approached from a lower. The curves
in Fig. 5 bring out this point, in that one curve, obtained with a sample that
was not previously conditioned by drying, is above the other three. This test

FIG. 6. *Moisture content gradients through sanded fibreboard samples.*

was made in May so that the laboratory relative humidity would be high; this resulted in a large initial moisture content and an approach to equilibrium from the high moisture side.   It has been sometimes noticed with other samples that there was a slight inflection in the middle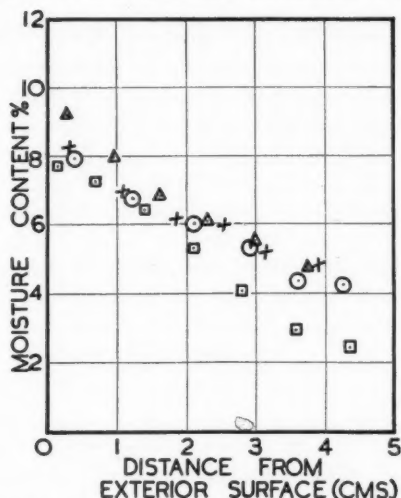 of the curve.   This is most probably due to the fact that the moisture content was initially at this point.   Equilibrium in the case of the fibreboard on the low humidity side of this point would be approached by desorption, while for the fibreboard on the high humidity side the approach would be by absorption.   In most cases the samples were conditioned by heating in a furnace until bone dry.   It was, however, impossible to prevent the absorption of a small amount of moisture from the laboratory atmosphere during mounting.   There is also a certain exchange of moisture between the sample and the atmosphere during the time in which the sample is being cut up.   It is probably a combination of these two effects that results in the slight curl that is seen at the end of the curves for most samples. Originally this slight upturn was thought to be the result of the difference in structure in the surface layers of the fibreboard.   That the fibres are here arranged parallel to the surface rather than at random as in the bulk of the material has been well established (2, 4).   If the resistance of the fibreboard to moisture movement were different in these surface layers a change in the slope of the moisture gradient curve would be expected near the surfaces. In order to determine if a difference in structure was responsible for this effect two samples were measured in the reversed position, i.e., with the screen side out.   These are shown in Fig. 5.   The surface layers were also removed from several samples and the moisture content was determined under those conditions.   The curves obtained for the latter are shown in Fig. 6.   The end effects are still evident in both cases; this indicates that the differences in

structure do not constitute the predominating factor. The inflection in the centre of the curve is very pronounced in these latter tests.

Another point to be noticed from these curves is that the moisture content does not appear to approach zero at the lower surface of the sample. Thus the curves in Fig. 5 indicate that the moisture contents run from about 9% on the moist side to a point probably between 2.5 and 3.0% on the dry side. This bears out the conclusion reached from the investigation on the change of resistance with thickness, that there was a residual resistance from the surface of the sample to the calcium chloride. In those measurements it was found that this resistance was approximately 0.01. Assuming that the total resistance of a 2-in. fibreboard is about 0.09, about 1/10 of the vapour pressure drop is in the cell itself. This would mean that the relative humidity at the lower surface of the cell would be 7.5%, which represents a moisture content of about 1.75%.

Within the range covered by these moisture contents the relation between moisture content and relative humidity is fairly linear. Since the experiments were carried out at constant temperature, this means that under these conditions the moisture content is proportional to vapour pressure and the curves do not differentiate between the two expressions for Fick's law. They do, however, give a clearer picture of the mechanism of moisture movement, and in the next section these measurements will be extended to include moisture transpiration with a temperature gradient through the sample.

Transmission of Moisture with Reversed Moisture Content Gradient

Since the moisture content of a hygroscopic material depends only on the relative humidity, it is possible by suitably adjusting the temperatures and vapour pressures on two sides of a sample to have a vapour gradient across the sample in one direction and the moisture content gradient in the opposite direction. A measurement of the amount of moisture transmitted under these conditions will determine the relative importance of moisture content and vapour pressure in moisture transmission.

An experiment of this nature has been attempted. The set-up is shown in Fig. 7. The cell plus fibreboard sample is set in a recessed metal block that can be heated by means of a coil of nichrome wire. The depth of the recess is such that the top of the metal block is on the same level as the bottom of the fibreboard. The fibreboard rising above the top of the metal block is surrounded with a ring of fibreboard to prevent lateral loss of heat, and the whole arrangement is packed in rock wool. Since metal is a good conductor of heat there will be no temperature gradients in the metal block. The temperature of the block was measured by means of a thermocouple attached to the surface of the metal immediately under the centre of the cell. With this arrangement the solution within the cell should be at a temperature equal to that of the metal block as given by the thermocouple. The vapour pressure within the cell will depend on the temperature and nature of the solution.
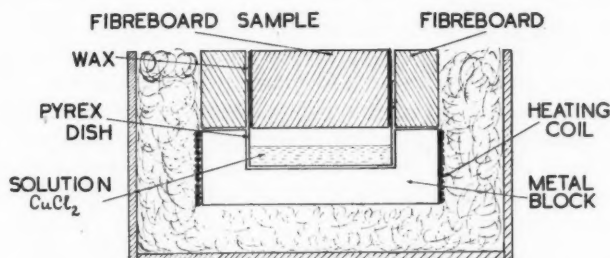
FIG. 7 *Arrangement of apparatus to determine moisture gradient through fibreboard sample with a temperature difference across the sample.*

It can be assumed that this is also the temperature of the bottom surface of the fibreboard, and that the temperature of the top surface is that of the air in the humidified chamber. The temperature gradient through the fibreboard can be assumed to be linear. On the assumption that the temperature of the surfaces of the fibreboard are respectively equal to the air temperatures on the two sides of the sample, the surface coefficients are being neglected, but the error introduced by this assumption should be negligible for the purpose.

The apparatus described above was placed in a chamber in which the temperature was held constant at 85.5° F. and in which the humidity was maintained at 75% by means of a saturated sodium chloride solution. A saturated solution of cupric chloride was placed within the cell and the current in the heating coil on the metal block was adjusted so as to give a temperature of 102° F. A saturated cupric chloride solution at 102° F. has a vapour pressure of 35 mm. of mercury (Landolt and Börnstein Tabellen). This represents a relative humidity of 67%. Outside the cell the vapour pressure is 23.5 mm. of mercury. Thus, under these conditions there is a vapour pressure gradient decreasing from the cell to the exterior, and a relative humidity gradient decreasing from the exterior to the cell. A change of weight of the cell over a period of time will, therefore, immediately show whether it is the vapour pressure or the relative humidity that is the predominant factor.

This experiment was carried out on two separate samples of 2 in. fibreboard, cut from the same board. In both cases the cell lost weight over a period of several days. The results of these tests are summarized below.

TABLE IV

	External temp., °F.	External pressure, mm. Hg.	Internal temp., °F.	Internal pressure, mm. Hg.	Diffusance
Sample I	85.5	23.5	103.6	36.4	16.2
Sample II	85.5	23.5	102.5	35.0	14.0

A similar sample cut from the same board and tested under the usual conditions, where there is no temperature gradient and the vapour pressure difference is that given by 75% relative humidity on one side and 0% on the other, gave a diffusance of 14.2 gm. per 24 hr. per sq. metre per mm. of mercury. The agreement between this figure and that obtained with the two samples above is such that there can be no doubt (i) that it is the vapour pressure gradient and not the moisture content that is the driving force in moisture movement in fibreboard, and (ii) that a direct quantitative relationship holds between the amount of water vapour transferred and the vapour pressure difference across the sample.

As a further check on this theory each of these samples was, at the conclusion of the test, cut up into small pieces and the moisture content gradient through the sample obtained by weighing. The results for the two samples are given in Table V, together with those for an additional sample whose diffusance was not determined.

TABLE V

Sample I Thickness, 4.990 cm.		Sample II Thickness, 5.042 cm.		Sample III* Thickness, 5.072 cm.	
Distance from outside surface, cm.	Moisture content, %	Distance from outside surface, cm.	Moisture content, %	Distance from outside surface, cm.	Moisture content, %
0.161	8.86	0.515	9.34	0.371	9.74
0.825	10.10	1.740	9.41	1.254	9.76
1.679	10.02	2.826	9.22	2.129	9.50
2.523	9.83	3.684	8.97	3.007	9.29
3.454	9.30	4.605	8.64	3.884	8.82
4.509	8.83			4.734	8.59

*Conditioned at 75% relative humidity.

These results have been plotted in Fig. 8. There is some difference in the three cases, the moisture contents of Sample I being in general greater than those of Samples II and III. The explanation of this is not evident, but it is most probably bound up with the hysteresis effect. If it is assumed that the temperature and vapour pressure gradients are linear through the samples, it is possible to calculate the moisture content. This has been done and the calculated curve has been drawn in the figure. The experimental points agree nicely with the calculated curve for the low humidity side but towards the outside they fall rather rapidly. This can be accounted for by supposing that the sample loses moisture between the time it is taken from the chamber and the time when finally the sections are placed in the weighing bottles. Under these conditions the outer section would be expected to lose more moisture than the others owing to its exposed position. In the case of Sample III, which was conditioned at 75% relative humidity, extra care was taken to ensure that as little moisture as possible was lost, and in this case the effect at the outside is not nearly so pronounced. In this type of work
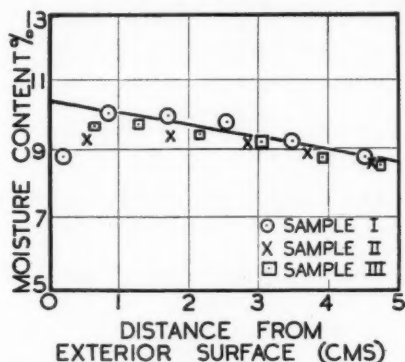
FIG. 8. *Moisture content gradients through fibreboard samples obtained with temperature difference across samples.*

some uncertainty is always present owing to the hysteresis in the relative-humidity–moisture-content curve. There is always an element of doubt as to whether the desorption or adsorption curve should be used. No matter how much care is taken to condition the sample before the test, small variations in the humidity are bound to occur, with the result that the final condition of the sample may be anywhere between the adsorption and desorption curve. On the whole, the agreement between theory and experiment is such that there is no reason to believe that the diffusion is not proceeding according to Fick's law. It is especially instructive to note that the moisture contents decrease towards the inside of the cell, while in every case there was a loss of moisture, showing that the moisture content gradient does not effect the transpiration of moisture under these conditions.

Acknowledgment

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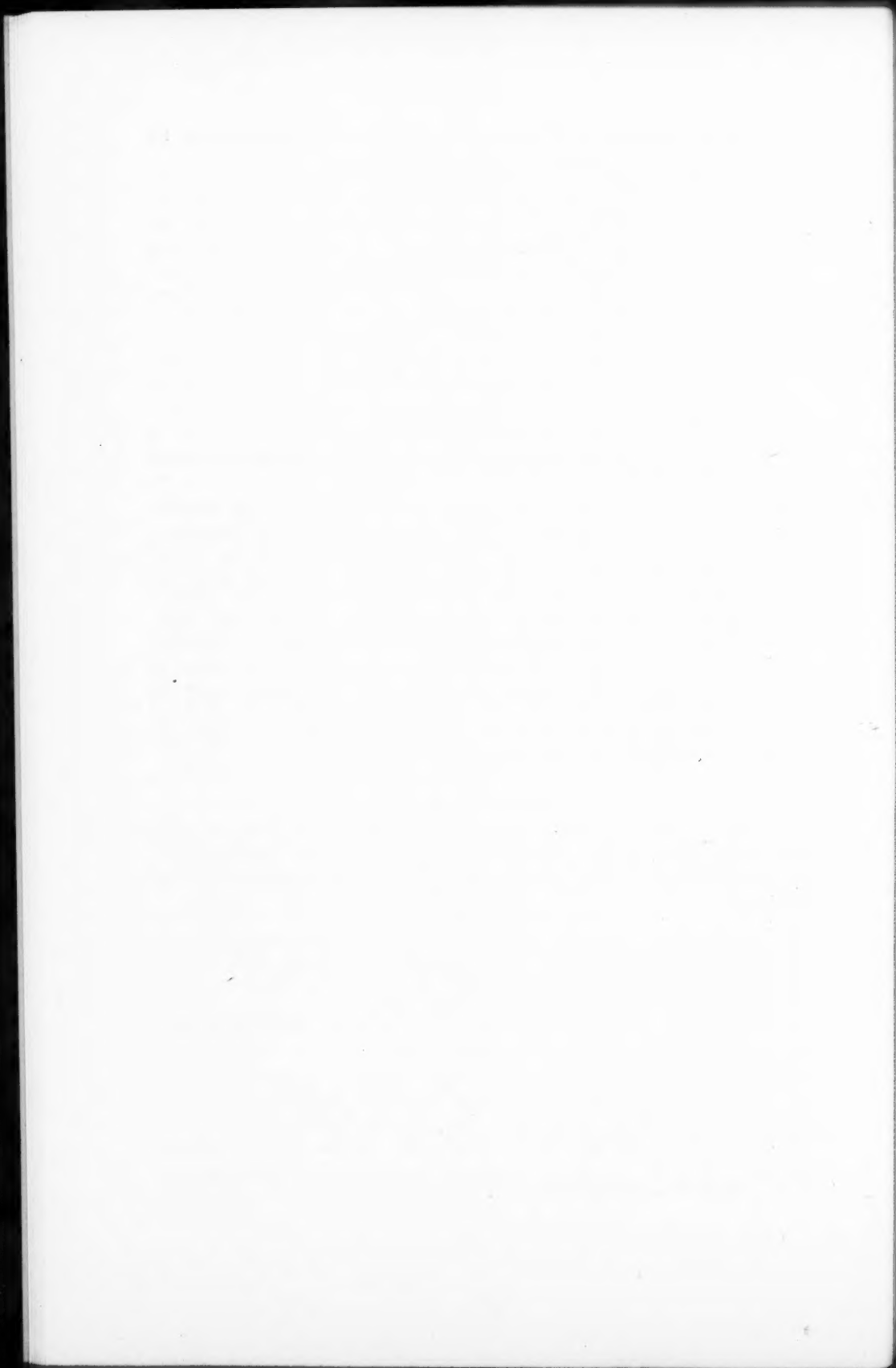
THE DETERMINATION OF SMALL AMOUNTS OF FLUORINE IN WATER[1]

BY OSMAN JAMES WALKER[2] AND GORDON ROY FINLAY[3]

Abstract

In the survey of Alberta waters in which fluorine content is compared with the prevalence of mottled teeth, the titration method and the colorimetric method for determining fluorine have not always given comparable results. Good results with the titration method are obtained when distillation is carried out with perchloric acid instead of with sulphuric acid. It was found that the colorimetric method is affected by more than 2 p.p.m. of phosphate, aluminium, or ferric ions, and by over 120 p.p.m. of sulphate ions. Moderate amounts of manganous, ferrous, silicate, chloride, and sodium ions do not interfere. When the water contains over 2 p.p.m. of phosphate, aluminium, or ferric ions, or if the water is coloured, the titration method is used. A scheme for correcting for sulphate ions is proposed. The titration method and the colorimetric method used in this laboratory for determining fluorine in waters are given in detail.

Of the methods reported for the determination of fluorine in natural waters, the colorimetric method developed by Sanchis (13) and the Willard and Winter (18) titration method adapted for micro-analysis by Boruff and Abbott (4) and by Armstrong (2, 3) have been modified (17) and used in this laboratory. The first method depends on the bleaching action of fluorides on the lake formed by sodium alizarin sulphonate and zirconyl nitrate in which the zirconium is undoubtedly tied up as either ZrF_5^-, ZrF_6^{--}, or ZrF_7^{---} (9). The second method consists of distilling the fluorine as fluosilicic acid from a solution containing excess of sulphuric acid and silica, adding sodium alizarin sulphonate and titrating with a standard solution of thorium nitrate.

In the extensive examination of Alberta natural waters for fluorine content (15, 17) and also in the determination of fluorine in fluorine removal experiments (16) which were in progress it was found that results were not always consistent. It was believed that either or both of the methods were affected by dissolved substances in the water, so it was deemed advisable to tabulate the variation in dissolved salt content that might be met with in the waters of Alberta.

Table I lists the range of constituents which has so far been found in Alberta drinking waters.

TABLE I

COMPOSITION OF ALBERTA WATERS (P.P.M.*)

Total solids	200 – 10,000	Fe^{++}	0 – 100†
Loss on ignition	0 – 600	Fe^{+++}	0 – 2
Total hardness	0 – 1,000	Colloidal iron compounds	0 – 40
SO_4^{--}	0 – 8,000	Mn^{++}	0 – 2
Cl^-	0 – 200	PO_4^{---}	0 – 25
Alkalinity	0 – 1,200	SiO_2	0 – 35
Alkali bicarbonates	0 – 1,500	I^-	0 – 0.4
Aluminium and iron oxides	0 – 100	F^-	0 – 5

* *P.p.m. = parts per million parts of water.*
† *Over 2 very rare.*

Borates, lithium, sodium, and potassium salts as well as small amounts of ammonia, nitrites, and nitrates are also present.

Because of the great diversity in the composition of natural waters, it was decided to attempt to determine the elements that interfered in the determination of fluorine and to devise modifications in the methods of analysis so that satisfactory results would be obtained.

(a) Titration Method

Many investigations have been reported recently on the titration method (5, 8, 10, 11, 12). Although such ions as Cl^-, SO_4^{--}, and PO_4^{---} are known to interfere with the method, the modifications that have been proposed, especially those involving double distillation, first from sulphuric acid and then from perchloric acid, and titration in a solution containing a satisfactory buffer in the presence or absence of alcohol, seem to give results that are consistent and accurate even for large amounts of these ions. Although chlorides distil over with fluorides in these modified methods, the amounts present in Alberta waters are not sufficient to cause interference (8). In the light of the experience of the present authors and of other investigators the procedure for the determination of fluorine in waters that has been followed in these laboratories is as follows:

Procedure for determining fluorine in waters by the titration method. The size of sample used is such that approximately 0.2 mg. of fluorine is present. This is made alkaline to phenolphthalein with 0.2 N potassium hydroxide, concentrated to 50 cc. and transferred to a 250 cc. Claissen, Pyrex, distilling flask along with 20 cc. of concentrated sulphuric acid and some glass beads.

If more than 2 p.p.m. of phosphate is present, 30 cc. of 60% perchloric acid is used in place of the sulphuric acid. Care must be taken if organic matter is present, and the perchloric acid must not be allowed to come in contact with rubber connections. When phosphates are very high, a double distillation, first with sulphuric acid followed by perchloric acid, is required.

The flask is fitted with a two holed rubber stopper through which pass a thermometer and a dropping funnel connected to a capillary tube so that water may be added from time to time. The thermometer and the capillary

tube extend into the liquid.   A water condenser is attached to the outlet tube of the flask.

The flask is heated, distillation begins about 110° C. and is continued until 75 to 100 cc. of distillate is collected, water being added from time to time to keep the temperature of the liquid in the flask just below 135° C.   In this method the fluorine is volatilized as fluosilicic acid.   Interfering ions remain in the flask although when sulphuric acid is used some sulphates, phosphates, and nitrates distil over.   With perchloric acid, phosphates are retained in the flask while the amount of sulphates is so small that they do not interfere.

The distillate is made alkaline to phenolphthalein with 0.2 N potassium hydroxide and concentrated to either 20 or 50 cc., the volume depending on whether titration is to be in alcoholic or water solution.

When the titration is carried on in the presence of alcohol, 20 cc. of ethyl alcohol and three drops of a 0.5% aqueous solution of sodium alizarin sulphonate to serve as indicator are added to the concentrated distillate.   The solution is titrated with 0.2 N hydrochloric acid until the colour changes from red to yellow.   To fix the pH of the solution, 2 cc. of the buffer solution proposed by Hoskins and Ferris (8) is added.   The buffer solution is made by mixing two parts of M monochloracetic acid and two parts of M sodium chloracetate with one part of water, and is thus 0.4 M with respect to both acid and salt.   Titration is now carried out in a Nessler tube with standard 0.02 N thorium nitrate solution from a 10 cc. microburette to the appearance of a faint, permanent reddish coloration.   The thorium nitrate solution is standardized against 0.02 N sodium fluoride.   It is necessary to run a blank each time on distilled water treated in the same manner in order to determine the amount of thorium nitrate solution required to form the thorium lake. The volume of thorium nitrate solution required for the blank, usually 0.03 to 0.05 cc., is subtracted from the total volume used.   Calculations are based on the size of sample and net standard thorium nitrate used.

Titration in water solution is carried out on the 50 cc. of concentrated distillate.   To this are added three drops of the indicator and the solution is titrated to a yellow with 0.2 N hydrochloric acid.   Buffer solution (3 cc.) is added and the solution titrated as before with the standard thorium nitrate. Blanks are also run.   Calculations are made as before.

In the titration of standards, better results are obtained in water solutions but when waters of unknown composition are titrated, alcoholic solution has been found to be preferable.

(b) The Colorimetric Method

It was felt that most discrepancies in the values obtained were in the colorimetric method, so a great deal of attention was paid to possible interference by the elements that might be present in water.   It is of great importance that the colorimetric method give good results as it is so much more rapidly carried out than the titration method.

Series of experiments were run in which varying amounts of fluoride ion and the ion under consideration were added to distilled water. The ions were used in concentrations that would be met with in natural waters, as shown in Table I. In all cases fluorine was added as sodium fluoride, the proper volume of a dilute standard solution being used. Concentrations in all cases are expressed in p.p.m.

Effect of Mn^{++}. Manganous salt in amounts met with in natural waters do not alter the apparent amount of fluoride when this method of analysis is used. However, when concentrated manganous solutions are used, the indicator is destroyed.

Effect of Al^{+++}. Accurate results may be obtained with this method when the aluminium ion content is less than 5 p.p.m. When the concentration is greater than this, results for fluorine determinations are low, most likely owing to the tying up of fluorine as AlF_6^{---}.

Effect of Fe^{++}. Ferrous ions have little effect in the determination of fluorine up to 10 p.p.m. Readings tend to be high.

Effect of Fe^{+++}. When the Fe^{+++} content is over 3 p.p.m. the indicator is affected in such a way that no readings can be obtained. For some unknown reason the colour of the solutions is completely destroyed.

Effect of Silicate. Silicate was added as sodium silicate. It has no effect on the analysis even when present in quantities as great as 80 p.p.m. Interference by silicates does not seem to be as serious as some investigators imply (7, 13).

Effect of Cl^-. Chloride was added as magnesium chloride. Even up to 1000 p.p.m., chlorides have no effect on the method. This is according to expectations as hydrochloric acid is always added at the same time as the indicator. Undoubtedly there could be an effect if quantities of chloride ion corresponding to the amount of hydrochloric acid added were present.

Effect of Na^+. The effect of sodium ions on the method was determined by supplying the sodium either as sodium chloride or as sodium carbonate. The sodium ion does not interfere with the determination.

Effect of Phosphates. It was found that the effect of phosphates was extremely irregular. In some cases high values were obtained while in others the values were low. It was not possible to get concordant results. Because of the lack of agreement, samples of water containing over 2 p.p.m. of phosphate as P_2O_5 are analysed by the titration method.

Effect of Sulphates. It has been known that sulphates have an effect on the sodium-alizarin-sulphonate–zirconyl-nitrate indicator similar to that of fluorides. The addition of 2 cc. of 3 N sulphuric acid is made in the regular method so that the effect of varying amounts of sulphates in natural waters met with in ordinary cases will be minimized. Some waters are, however, so rich in sulphates that the amounts present are comparable to those supplied by the sulphuric acid. When this is the case the values obtained for fluorine

are higher than they should be. Some of the values obtained are shown in Table II. In this series the sulphate was added as sodium sulphate.

TABLE II

INFLUENCE OF SULPHATES ON THE DETERMINATION OF FLUORINE

F⁻ present, p.p.m.	Sulphates added, SO_4^{--}, p.p.m.							
	120	300	480	600	1200	1800	2400	3600
	F⁻ found, p.p.m.							
0.0	0.0	0.1	0.2	0.2	0.6	0.7	0.9	1.1+
0.2	0.3	0.3	0.4	0.4	0.7·	0.8	1.1	
0.4	0.4	0.5	0.6	0.7	0.8	1.1	1.2	
0.6	0.6	0.7	0.8	0.9	1.1	1.3	1.5	
0.8	0.8	0.9	1.0+	1.1	1.2	1.5		
1.0	1.0	1.0+		1.2	1.4			
1.2	1.2	1.5						

As the corrections needed to be applied with large quantities of sulphates were so high, it was decided to see if there would be any advantage in using a smaller quantity of sulphuric acid than had previously been proposed by Sanchis (13) when he devised this method of analysis. In place of the 2 cc. of 3 *N* sulphuric acid used in the regular method, smaller and larger amounts were taken and used with water containing varying concentrations of fluorine. The results of these tests are shown in Table III. The sulphuric acid was actually 3.25 *N*, and the addition of 1 cc. of this to 100 cc. of water corresponds to 1500 p.p.m. of sulphate ion. It must be remembered that the values given are obtained by comparison with standards to which had been added 2 cc. of 3 *N* sulphuric acid.

TABLE III

INFLUENCE OF SULPHURIC ACID ON THE DETERMINATION OF FLUORINE

F⁻ present, p.p.m.	Sulphuric acid added, SO_4^{--}, p.p.m.									
	0	1560	1900	2250	2700	3300	3750	4500	5250	6000
	F⁻ found, p.p.m.									
0.0									1.4	
0.2					0			1.2	1.5	2.0
0.4				0				1.4		
0.6					0.4	0.7	0.9	1.5		
0.8			0	0.3						
1.0		0			0.75					
1.2			1.4	0.8						
1.5		0.4	0.8	1.0	1.2					
1.6				1.1						
1.8		0.7		1.4						
2.0		0.9	1.3	1.5						
2.3		1.25								
2.5		1.3		2.0						
3.0	0.0	1.5	1.5	+2						
4.0	0.4		+2.0							

The present range of the colorimetric method is from 0 to 1.5 p.p.m. of fluorine.   If the sulphuric acid content of the unknown and standards were reduced to 1 cc. the range of colour shown by the figures in Column 3 would be obtained.   The method would then be suitable for the colour range for a fluorine content of 1.0 to about 2.5 p.p.m. of fluorine.   If 1.5 cc. of sulphuric acid were used, the fluorine content to be measured by the methods would be from 0.4 to 2 p.p.m. (Column 5).   From these considerations it was felt that there is no advantage in changing the amount of sulphuric acid used in the method.

Scott and his co-workers (14) and Dean and Elvove (6) have investigated the interference of sulphates and have applied corrections for their presence. Corrections for sulphates are also embodied in the Standard Methods of Analysis of the American Public Health Association (1).   By referring to Table II it can be seen that small amounts of sulphates do not interfere, but as the sulphate content rises the apparent amount of fluorine increases. Roughly speaking, the correction to be applied is approximately 0.1 p.p.m. of fluorine per 300 p.p.m. of sulphate in lower concentrations but less in higher concentrations of fluorine.   The results in Table II showing the relationship between fluorine added and fluorine found are expressed graphically in Fig. 1.   A separate graph is given for each concentration of sulphate. It will be seen that the graphs are parallel straight lines.   In cases where fluorine found has been less than 1.5 p.p.m. the lines have been extrapolated to that value.   The graph for 120 p.p.m. of added sulphate falls on the graph

Effect of Sulphates on Determination of Fluorides

Fig. 1.
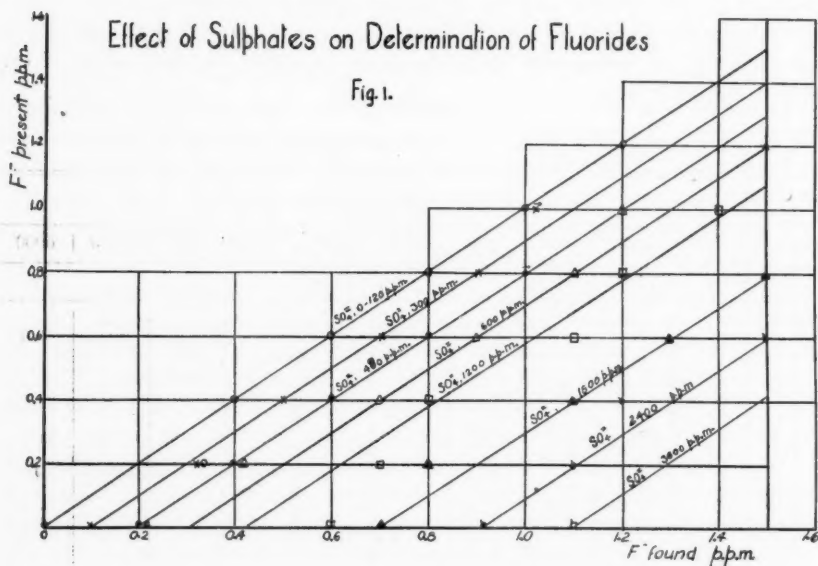
for no added sulphate.   As the sulphate content rises, the greater is the distance
of the graph from the medial line and thus the greater the error in reading.

It can be seen that this figure is very useful in the colorimetric method for
the determination of fluorides if the sulphate content of the water is known
and if not enough ferric ion, aluminium ion, or phosphates are present to
interfere.   It must be remembered that the colorimetric method is good only
up to 1.5 p.p.m. of fluorine, so that if used for larger concentrations, smaller
volumes are taken and diluted with distilled water to the 100 cc. volume
regularly used.   If a chart based on Fig. 1 is available the correction for sul-
phates can be made as follows.   The uncorrected amount of fluorine is deter-
mined.   The chart is now referred to, and use is made of the graph nearest to
the sulphate content of the water (or the diluted sample).   The correct
amount of fluorine can then be read from the ordinate.   This may be multi-
plied by an appropriate factor to obtain parts per million if the sample has
been previously diluted.

The fluorine content of a number of Alberta waters has been calculated
by this method.   Table IV contains these data.   In Column 3 is given the

TABLE IV

FLUORINE CONTENT OF WATER

Water No.	Place	SO_4^{--}	Fluorine content		
			Titrimetric	Colorimetric	Colorimetric corrected for SO_4^{--}
411	Champion	1200	1.9	2.4	1.9
458	Claresholm	3300	0.4	1.2	0.2
485	Killam	3200	0.3	1.0	0
489	Cochrane	150	0.7	1.0	0.9
537	Calgary	1100	0.6	1.0	0.6
571	Macleod	65	2.4	3.7	3.7
589	Vegreville	5600	0.2	1.2	0
615	Edmonton	500	1.2	0.7	0.5
620	Brant	300	4.3	4.2	4.1
644	Cummings	50	1.5	1.4	1.4
645	Wrentham	1040	0.4	1.5	1.1
646	Kitscoty	400	0.9	1.5	1.3
647	Waskatenau	260	0.5	1.2	1.0
650	Barons	8000	0.5	1.8	0 ?
663	Acme	1080	1.0	0.9	0.5
680	Maclennan	2200	0.1	0.6	0
684	Nanton	1800	1.1	1.9	1.2
685	Vulcan	430	1.6	2.0	1.8
695	Kingman	3000	0.3	0.9	0
702	Brant	200	4.6	4.4	4.4
703	Brant	380	1.5	1.8	1.7
704	Brant	350	2.7	2.4	2.3
712	Cayley	1540	1.4	1.7	1.2
720	Parkland	100	2.7	2.7	2.7
728	Fleet	2770	0.2	1.1	0.1
731	Beaver Lodge	550	0.6	1.5	1.2
739	Granum	340	4.6	4.2	4.1

sulphate content in parts per million as determined gravimetrically, in Column 4 the fluorine determined by the titration method, in Column 5 the amount of fluorine found by the colorimetric method, and in the last column the values calculated from Column 5 by using the graphs in Fig. 1. It will be seen that these corrected values agree fairly well with those found by means of the titration method, although there are some large discrepancies such as in Runs 571, 615, 645, and 731. So far, no plausible explanation has been presented for these differences. In the light of the information in Tables II and III, values for fluorine content are now obtained regularly by determination of sulphate content followed directly by the colorimetric method, which is corrected by the use of the chart in Fig. 1.

In the light of the investigations heretofore listed, all uncoloured samples of water that are low in ferric ion, aluminium ion, and phosphates are analysed by means of the colorimetric method and the correction for sulphate is applied. A detailed description of the method follows.

Procedure for Determining Fluorine in Waters by the Colorimetric Method

Only uncoloured samples can be analysed by means of this method, although some coloured waters may be decolorized by activated charcoal (Norite) and give good results. Samples containing over 2 p.p.m. of phosphates, aluminium, or ferric ion are analysed by means of the titration method. The sulphate content of samples to be analysed by means of the colorimetric method is determined before proceeding with the calculation of fluorine content.

For the determination of fluorine, 100 cc. of water is used and to this are added, 2.0 cc. of 3 N hydrochloric acid, 2.0 cc. of 3 N sulphuric acid, and 1.8 cc. of indicator. The indicator contains 0.17 mg. of sodium alizarin sulphonate and 0.87 mg. of zirconyl nitrate, $ZrO(NO_3)_2 . 2H_2O$, per cc. The solution is heated to boiling, allowed to stand overnight and compared in Nessler tubes with standards of the same volume, containing 0.0, 0.2, 0.4, 0.6, 0.8, 1.0, 1.2, and 1.5 p.p.m. of fluorine added as sodium fluoride, which have been treated in the same manner. The uncorrected fluorine content is read off directly. In cases where the fluorine content appears to be greater than 1.5 p.p.m., new determinations must be made using smaller samples, 50 cc., 25 cc., or less, and diluting with distilled water to 100 cc. before adding the acids and the indicator.

The uncorrected values are now corrected for sulphates by the use of Fig. 1, the dilution of the sulphate, if samples less than 100 cc. have been used, being taken into account. The corrected value for the fluorine content is then multiplied by the appropriate factor if less than 100 cc. of water has been used, and the results are now in parts per million.

Acknowledgment

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ÉTUDES PHYSICO-CHIMIQUES SUR LES CARBONATES ALCALINS

I. RECHERCHES SUR L'ACTIVITÉ DES IONS-HYDROGÈNE DANS LES SOLUTIONS AQUEUSES DE CARBONATES ALCALINS[1]

PAR LÉON LORTIE[2] ET PIERRE DEMERS[3]

Extrait

On a mesuré, au moyen de l'électrode à hydrogène, le pH de solutions des carbonates neutres de sodium et de potassium, à 25° C. Pour des concentrations moyennes (de 0.005 à 1 M) la relation entre pH et log M est à peu près linéaire. A toute concentration, le pH est plus élevé pour le sel de potassium, ce qui s'accorde avec la valeur des coefficients d'activité des sels de sodium et de potassium.

État de la question

Le mécanisme de l'absorption du gaz carbonique par des solutions de carbonates alcalins est encore mal connu. Les nombreux auteurs qui se sont occupés de mesurer la vitesse de cette réaction présentent des résultats apparemment contradictoires et les tentatives d'explication que certains d'entre eux ont proposées s'opposent presque autant que les mesures. C'est que plusieurs facteurs peuvent modifier les conditions du phénomène qui se passe lorsque le gaz carbonique vient en contact avec la solution de carbonate alcalin.

La discordance des mesures peut s'expliquer par le choix des appareils qui sont de deux types.

Dans le premier, la valeur du rapport de la surface d'absorption à la masse liquide est grande: colonnes à contre-courant, tours remplies de cailloux ou de segments destinés à accroître cette surface. Comme, dans ces appareils, la teneur du liquide en gaz absorbé varie rapidement et que le gaz est en contact assez prolongé avec une liqueur de concentration inégale en chacun de ses points, on ne mesure que la vitesse *moyenne* d'absorption.

Le second type, qui comprend les appareils où on laisse tomber des gouttes de liquide dans un gaz, ou monter des bulles gazeuses dans le liquide absorbant, et les burettes de Bunte, est caractérisé par une faible valeur du rapport déjà mentionné. Ce sont plus spécialement des appareils d'étude et de laboratoire, par opposition aux premiers qui sont surtout réalisés dans l'industrie. On s'en sert, parce que la concentration en gaz absorbé varie plutôt lentement, pour déterminer la vitesse *initiale* d'absorption.

Avec un appareillage du premier genre, Williamson et Mathews (24), Payne et Dodge (17), Hatta (8), Harte et Baker (7) ont trouvé que la con-

centration en carbonate est à peu près sans effet sur la vitesse d'absorption. Par ailleurs, avec des montages du second genre, Ledig et Weaver (13), Riou et Cartier (18, 19, 20), Davis, Thomson, et Crandall (2), Hitchcock et Cadot (11) aboutissent à des conclusions différentes: la vitesse augmente jusqu'à un maximum à mesure que croît la teneur en carbonate alcalin puis décroît ensuite pour des concentrations salines plus élevées. La vitesse la plus grande est obtenue, avec les carbonates de sodium ou de potassium, pour une concentration voisine de la normalité.

Tous ces auteurs ont noté l'influence favorable de l'agitation. Riou et Cartier (19, 20, 21) ont aussi obtenu des résultats remarquables en ajoutant aux solutions de carbonates diverses substances organiques solubles dans l'eau et jettent ainsi un jour nouveau sur la question. Payne et Dodge (17), à cause du type d'appareils qu'ils utilisaient, n'ont pu reproduire les effets constatés par Riou et Cartier (20, 21). Mais Hitchcock (10) y est parvenu sans difficulté en se servant d'un système du second type.
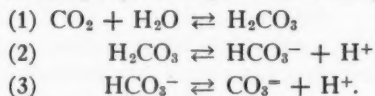
La viscosité de tous les mélanges étudiés, carbonates seuls ou additionnés de substances organiques, s'accroît avec la concentration, ce qui montre que la vitesse de solution de l'anhydride carbonique n'est pas contrôlée uniquement par le processus physique de la diffusion qui dépend de la viscosité. C'est la conclusion à laquelle parviennent Riou, Cartier et Lortie (20, 21, 22). Il ne semble pas douteux, toutefois que, dans une théorie générale du phénomène, il faille tenir compte de ce facteur.

On n'avait guère considéré jusqu'ici deux éléments du problème: l'activité ionique du milieu et l'existence possible de composés autres que le carbonate et le bicarbonate alcalins dans la solution, et de nature probablement complexe, au moins lorsque la vitesse d'absorption est plus ou moins augmentée par la présence de corps étrangers.

Les solutions de carbonates alcalins sont, d'autre part, fortement hydrolysées et nous devons nécessairement tenir compte de toutes les réactions ioniques responsables de cet état de choses.

Il est aujourd'hui démontré que le gaz carbonique en solution n'est pas hydraté entièrement et que la vitesse de cette hydratation est finie.

Au contact de l'eau, le gaz carbonique se dissout, s'hydrate et s'ionise. Faurholt (3) a fait une étude très complète des réactions du gaz carbonique dissous. Le gaz carbonique peut réagir suivant un premier schéma:

$$(1) \quad CO_2 + H_2O \rightleftarrows H_2CO_3$$
$$(2) \quad H_2CO_3 \rightleftarrows HCO_3^- + H^+$$
$$(3) \quad HCO_3^- \rightleftarrows CO_3^- + H^+.$$

Ou bien suivant cet autre:

$$(4) \quad CO_2 + OH^- \rightleftarrows HCO_3^-$$
$$(3) \quad HCO_3^- \rightleftarrows CO_3^- + H^+.$$
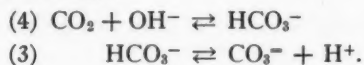
On peut admettre que les équilibres ioniques suivant les réactions (2) et (3) s'établissent très rapidement; la vitesse d'hydratation est définie par les réactions parallèles (1) et (4). Elle correspond à la transformation globale du gaz carbonique en molécules d'acide carbonique, ions HCO_3^- et CO_3^-. En solution très basique (pH > 10, par exemple), la vitesse suivant la réaction (1) est négligeable vis-à-vis de la vitesse suivant (4); si les conditions sont très éloignées de l'équilibre, on peut aussi négliger la vitesse de déshydratation correspondant à la formule (4) lue de droite à gauche; Faurholt (3) écrit alors:

$$\frac{d[CO_2]}{dt} = -k\,[CO_2]\,[OH^-]$$

Les crochets désignent les concentrations, t représente le temps, k une constante.

Dans les conditions—éloignées de l'équilibre—où l'on mesure une vitesse initiale d'absorption, au moyen d'un appareil du second type, la vitesse d'hydratation du gaz carbonique dissous est proportionnelle à la concentration de l'ion OH^-.

Il était donc intéressant de connaître la concentration, ou l'activité de l'ion OH^-, soit le pH des solutions de carbonates alcalins avec ou sans addition de corps organiques, et singulièrement de polyols qui, dans un autre domaine, se sont révélés de puissants agents de formation de complexes.

Quelques chercheurs ont étudié le pH des solutions de carbonate de sodium. Ces travaux étant assez anciens, nous avons jugé à propos de les reprendre. Les résultats de Kiehl et Loucks (12, p. 98) parurent alors que notre travail était déjà commencé.

Quant au carbonate de potassium, aucune donnée ne se trouvait dans la littérature. Nous avons effectué les premiers ces mesures dont nous rapportons plus loin les résultats.

Mesures de pH dans les solutions aqueuses de carbonates alcalins

Divers auteurs ont fait des mesures, à l'aide d'une électrode d'hydrogène, sur des solutions de carbonate neutre de sodium. Frary et Nietz (4) et Menzel (16, p. 288) ont opéré à 25° C. Les mesures de Kiehl et Loucks (12, p. 98) ont été faites à 30° C. Walker, Bray, et Johnston (23) ont fait de telles mesures sur des mélanges de carbonate et de bicarbonate de potassium.

Produits chimiques et appareils

Nous nous sommes servis de carbonates alcalins Kahlbaum purs pour analyse. Le carbonate de sodium a été maintenu à 110° C. pendant plusieurs jours. Nous avons constaté qu'un échantillon de carbonate de potassium conservé pendant cinq mois à cette température retenait une proportion de bicarbonate suffisante pour diminuer le pH de 0.1 à 0.2 unité de pH dans certains cas. Il nous a fallu purifier le sel de potassium en le chauffant vers 250° à 300° pendant 15 min. Nous avons préparé quelques solutions dans une atmosphère d'hydrogène avec de l'eau bi-distillée bouillie. Nous n'avons pas observé de différences notables entre ces solutions et celles que nous avons préparées de la façon que nous allons décrire et que nous avons suivie généralement.

Un entonnoir à décantation est rempli d'air purifié par passage sur la chaux sodée. On introduit le sel sec par le haut, puis ensuite, par le robinet inférieur, de l'eau distillée une fois, bouillie et refroidie en présence d'air purifié lui aussi par passage sur de la chaux sodée. La concentration a été établie par titrage, au moyen d'acide chlorhydrique $0.1M$, en présence de phénolphthaléine à chaud ou de méthyl-orange à froid; les solutions les plus diluées ont été faites par pesées du carbonate et de l'eau. La concentration est connue à $\pm 0.3\%$ environ.

Nous nous sommes servis d'hydrogène électrolytique. Nous avons constaté que le passage de l'hydrogène sur du cuivre réduit chauffé au rouge sombre, pour enlever l'oxygène [Güntelberg (5)], accélère beaucoup l'obtention du potentiel d'équilibre dans les solutions de carbonates et aussi dans l'acide chlorhydrique $0.1M$, mais ne paraît pas affecter notablement la valeur finale du potentiel mesuré.

Le récipient pour l'électrode à hydrogène est celui de Clark (1, p. 293); entre chaque mesure, il a été démonté, lavé et les robinets graissés à nouveau. L'électrode de platine a été replatinée fréquemment.

En utilisant de façon convenable les robinets du récipient de Clark, nous avons pu le remplir d'hydrogène, le rincer puis le remplir de la solution à examiner et enfin, faire passer dans celle-ci un courant d'hydrogène sans que l'air extérieur vienne en contact avec la solution.

Mesures

La mesure de pH a été faite à 25° C. $\pm 0.5°$ dans une pièce à température constante ou dans un thermostat à air au moyen d'une pile du type suivant:

(A) Hg, Hg_2Cl_2, | KCl sat. || solution, | H_2, Pt (25° C.)
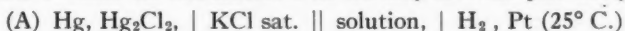
Pour la mesure des f.e.m., nous avons fait usage, soit d'un potentiomètre Leeds et Northrup, modèle portatif, soit d'un potentiomètre du type K.

On mesure d'abord la f.e.m. de la pile A contenant la solution étudiée; soit E volts la valeur obtenue. On remplace ensuite la solution étudiée, après nettoyage du récipient de Clark, par une solution d'acide chlorhydrique $0.1M$; soit E_{HCl} la valeur trouvée pour la f.e.m. En posant pH = 1.085 pour l'acide chlorhydrique $0.1M$, nous écrivons, avec Hitchcock et Taylor (9):

$$(5) \quad pH = -\log (H^+) = \frac{E - E_{HCl}}{0.05915} + 1.085.$$

L'électrode à hydrogène dans l'acide chlorhydrique $0.1\ M$ constitue donc l'électrode de référence finale à laquelle l'électrode au calomel est comparée*.

Nous avons pu répéter les mesures sur une même solution à 0.2 mv. près, en plus ou en moins.

Chaque point des courbes représentées sur la fig. 1 résulte d'au moins deux mesures concordant à 0.5 mv. La précision finale paraît être de l'ordre d'un millivolt, ce qui équivaut à 0.017 pH.

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* *En fait, Hitchcock suppose que la jonction entre l'électrode au calomel saturée et la solution est faite au moyen d'une solution de chlorure de potassium saturée à 22°, mais cela change assurément très peu aux valeurs de la formule (5), que de faire la jonction avec une solution saturée à 25°.*

Résultats

Les résultats des séries de mesures effectuées sur des solutions de carbonate de sodium dans l'intervalle de concentrations compris entre 0.000518 M et 2.096 M d'une part, et sur des solutions de carbonate de potassium entre 0.00075 M et 7.71 M d'autre part, sont réunis dans les tableaux I et II.

TABLEAU I

MESURES DU pH DE SOLUTIONS DE CARBONATE DE SODIUM À 25° C.

M	log M	pH	M	log M	pH
2.096	0.321	11.699	0.0212	$\bar{2}.327$	11.063
1.277	0.106	11.617	0.00833	$\bar{3}.921$	10.919
0.417	$\bar{1}.620$	11.453	0.00204	$\bar{3}.310$	10.612
0.1733	$\bar{1}.239$	11.357	0.000518	$\bar{4}.714$	10.274
0.0818	$\bar{2}.913$	11.254			
0.0414	$\bar{2}.617$	11.171			

TABLEAU II

MESURES DU pH DE SOLUTIONS DE CARBONATE DE POTASSIUM À 25° C.

M	log M	pH	M	log M	pH
7.71	0.887	(13.107)*	0.05909	$\bar{2}.772$	11.255
1.611	0.207	(12.024)*	0.05824	$\bar{2}.765$	11.274
0.813	$\bar{1}.910$	11.730	0.02797	$\bar{2}.447$	11.194
0.781	$\bar{1}.893$	11.728	0.01025	$\bar{2}.011$	10.975
0.3082	$\bar{1}.489$	11.514	0.00365	$\bar{3}.562$	10.781
0.26024	$\bar{1}.415$	11.478	0.00156	$\bar{3}.193$	10.593
0.20546	$\bar{1}.312$	11.451	0.00075	$\bar{4}.875$	10.401
0.06315	$\bar{2}.800$	11.270			

    * *Avec le récipient de Clark, on établit la jonction liquide en superposant la solution examinée à la solution saturée de chlorure de potassium. Cette dernière étant très dense, les deux liqueurs restent en général nettement séparées. Mais les solutions de carbonate de potassium de concentration supérieure à 1.6 M possèdent une densité presque égale, ou supérieure à celle de la solution saturée de chlorure de potassium. Il faut craindre alors l'introduction facile, par convection, de chlorure de potassium dans la solution de carbonate de potassium. Les mesures doivent se faire en laissant fermé le robinet de jonction, ce qui modifie la f.e.m. Les mesures aux deux concentrations supérieures consignées dans le tableau II sont sujettes à caution.*

    Il faudrait dans ce cas superposer la solution de chlorure de potassium, plus légère, à la solution de carbonate de potassium.

Ces données sont encore figurées par les courbes sur le graphique de la fig. 1. Les triangles sur cette figure représentent les calculs faits par le prof. D. I. Hitchcock, de l'Université Yale, et qu'il a eu la grande obligeance de nous communiquer, ce dont nous lui exprimons notre très vive reconnaissance. Ces calculs sont basés sur la valeur de K_2, la seconde constante de dissociation de l'acide carbonique, tirée de l'étude de MacInnes et Belcher (14 et 15), sur
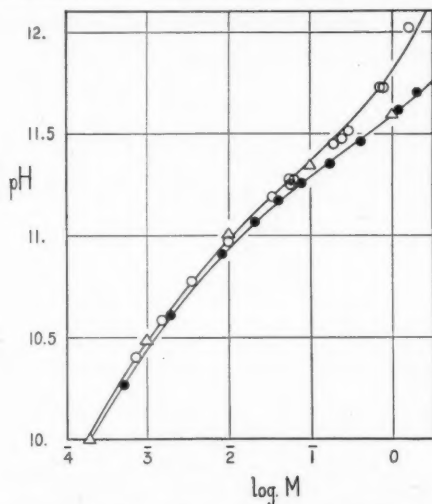
FIG. 1. *Courbes indiquant la variation du pH des solutions de carbonates alcalins en fonction de log M.* ○ *Solutions de carbonate de potassium.* ● *Solutions de carbonate de sodium.* △ *Calculs du prof. D. I. Hitchcock.*

la valeur de K_w, constante d'ionisation de l'eau, donnée par Harned et Hamer (6), et sur l'hypothèse que le potentiel de jonction est constamment nul.

On voit que nos propres résultats s'accordent, à une approximation de 0.02 pH environ, avec ces calculs, et par conséquent avec une valeur de la constante thermodynamique d'ionisation égale à $K_w/K_2 = 1.77 \times 10^{-4}$ pour 25° C.

Le tableau III et la fig. 2 se rapportent aux diverses données qui existent sur le carbonate de sodium.   Les valeurs du pH indiquées dans la troisième colonne sont tirées des f.e.m. E_h données par Frary et Nietz (4) pour 25° C. Les pH de la quatrième colonne sont donnés par Menzel (16) pour 25° C. Les résultats de Kiehl et Loucks pour 30° C. sont figurés dans la cinquième colonne.

TABLEAU III

VALEURS DU pH DE SOLUTIONS DE CARBONATE DE SODIUM SELON FRARY ET NIETZ, MENZEL, KIEHL ET LOUCKS

M	Log M	pH F. et N., 25°	pH M., 25°	pH K. et L., 30°
2	0.301	11.57	—	—
1.5	0.176	11.50	—	—
1	0.000	11.45	—	—
0.708	$\bar{1}$.850	11.41	—	—
0.5	$\bar{1}$.699	11.36	—	11.66
0.4	$\bar{1}$.602	—	—	11.62
0.3	$\bar{1}$.477	—	—	11.48
0.2	$\bar{1}$.301	11.26	11.54	11.41
0.1	$\bar{1}$.000	11.18	11.44	11.28
0.05	$\bar{2}$.699	11.00	11.37	11.16
0.02	$\bar{2}$.301	10.92	11.23	—
0.01	$\bar{2}$.000	10.82	11.11	—
0.005	$\bar{3}$.699	10.67	10.92	—
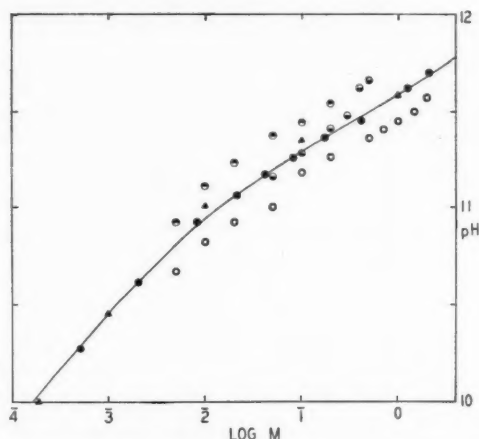
FIG. 2.   *pH — log M.   Solutions de carbonate de sodium.   Légende:* ○ *Frary et Nietz;*
● *Lortie et Demers;* ◐ *Kiehl et Loucks;* ◑ *Menzel;* ▲ *Hitchcock.*

Discussion des résultats

Il est à remarquer que, pour des concentrations moyennes, la relation entre pH et log M est à peu près linéaire.

Pour le carbonate de potassium, on peut écrire:

$$(6) \quad pH = \log \frac{1}{(H^+)} = 11.75 + 0.40 \log M \quad \text{pour } 0.002 < M < 1$$

On peut en tirer, puisque $K_w = 10^{-14}$:

$$(7) \quad (OH^-) = \frac{K_w}{(H^+)} = 5.63 \times 10^{-3} M^{0.40}$$

Semblablement pour le carbonate de sodium:

$$(8) \quad pH = 11.59 + 0.33 \log M \qquad \text{pour } 0.0005 < M < 1$$

$$(9) \quad (OH^-) = 3.9 \times 10^{-3} M^{0.33}$$

A toute concentration, le pH est plus élevé pour le sel de potassium.   Ce qui s'accorde avec ce que nous verrons dans un mémoire suivant, au sujet des coefficients d'activité, qui sont plus élevés pour le sel de potassium.

En effet, en partant des deux équations

$$(10) \quad K_w = (H^+)(OH^-)$$

$$(11) \quad K_2 = \frac{(CO_3^-)(H^+)}{(HCO_3^-)}$$

qui se rapportent respectivement à la dissociation de l'eau et à la seconde dissociation de l'acide carbonique, et en désignant par γ les coefficients d'activité, on peut obtenir l'équation suivante:

$$pH = -\log K_w + \log (OH^-)$$

$$(12) \quad pH = -\log K_w + \tfrac{1}{2} \log \frac{K_w}{K_2} + \tfrac{1}{2} \log [CO_3^-] + \tfrac{1}{2} \log \gamma_{CO_3^-} + \tfrac{1}{2} \log \frac{\gamma_{OH^-}}{\gamma_{HCO_3^-}}$$

Comme HCO_3^- et OH^- sont tous deux univalents, leurs coefficients d'activité sont voisins; le dernier terme du membre de droite de l'équation (12) est donc négligeable. On peut écrire:

$$pH = C + \tfrac{1}{2} \log [CO_3^=] + \tfrac{1}{2} \log \gamma_{CO_3}^=$$

D'autre part, le coefficient d'activité du carbonate augmente avec $\gamma_{CO_3}^=$. Admettons une dissociation totale du carbonate dissous. Pour une même concentration de celui-ci, le pH doit être d'autant plus grand que le coefficient d'activité du sel est plus grand.

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THE HEATS OF ADSORPTION AND WETTING OF MERCERIZED CELLULOSES BY SODIUM HYDROXIDE SOLUTIONS, WATER, AND METHYL ALCOHOL[1]

By J. L. Morrison[2], W. Boyd Campbell[3], and O. Maass[4]

Abstract

The heats of adsorption and wetting by aqueous sodium hydroxide, water, and methyl alcohol have been determined for celluloses mercerized at several different alkali concentrations. A quantity named the "heat of mercerization" has been determined, and it is considered to be a measure of the irreversible effects that distinguish mercerized from standard cotton cellulose, such as changed crystal lattice and enhanced internal surface. The extent of the latter change for the various mercerized celluloses has been shown by the heat of wetting measurements with water and methyl alcohol.

When cellulose is immersed in a strong alkali solution, it swells, heat is evolved, and the process called mercerization is said to take place. This phenomenon is of both practical and theoretical interest, and it is the purpose of this paper to assist in elucidating it.

The swelling of cellulose in alkali of sufficient concentration changes the crystal lattice of the cellulose, as shown by X-rays; in the case of sodium hydroxide these changes begin to appear at a concentration of 8 to 10%, and with increasing concentration above 10%, the old lattice disappears and a new one is visible. The lattice dimensions are unaltered in the direction parallel to the cellulose chains, but are altered (6) in the transverse direction. Clark (6) and Astbury (2) suggest different interpretations for the X-ray data, so that the significance of the changes is not certain.

Investigations by Neale (10) and others indicate that the product of mercerization exhibits an enhancement of properties, which, to a less extent, are characteristic of the original cellulose. The degree of enhancement or activity increases with the severity of the swelling treatment—in the case of sodium hydroxide, with the concentration up to 15%. The adsorption of water vapour is increased by mercerization (15), the amount depending on the concentration of the pretreating alkali, but at any one alkali concentration the percentage increase of water adsorption is constant over the whole range of vapour pressures. Urquhart and Williams (15) consider this to indicate a changed capacity but not intensity factor.

Ratios expressing the relative increase in the activity of mercerized cellulose towards different reagents are not in general the same. Thus (12) the so-

called "activation" ratios for technically mercerized cotton cloth compared with pure natural cellulose were: for water vapour, 1.25; for dilute sodium hydroxide, 1.77; and for alkaline potassium hypobromite, 1.56.

In this paper, measurements of the heats of adsorption on, and wetting of, mercerized cellulose are presented. The measurements involve the time of mercerization, the concentration under which mercerization is carried out, and the concentrations at which the heats of adsorption on mercerized cottons are measured. Neale (11) determined the heat of adsorption of sodium hydroxide on mercerized cotton prepared by treating standard cellulose with 15% sodium hydroxide solution. He found that the heat of adsorption of the 15% alkali was the same on the mercerized as on the untreated standard cellulose. Measurements presented in this paper do not substantiate this observation.

Concerning the heats of wetting of mercerized cotton by alcohol, a single reference is available in the literature. Chilikin (5) reports the heats of wetting of a mercerized cotton by water and by a 50% ethyl alcohol solution. In the present investigation the heats of wetting of celluloses, mercerized at several different concentrations of sodium hydroxide, by water and by absolute methyl alcohol are determined.

Experimental Technique and Materials

The apparatus and its manipulations in determining the heats of adsorption and wetting are the same as those described in two previous papers (8, 9). The mercerized cottons were prepared from standard cotton by immersion in sodium hydroxide solutions of several different concentrations from 5 to over 18%, usually for three hours. Subsequently, they were thoroughly washed, air-dried, and finally oven-dried at 100° C. Except for being in the mercerized state, these samples were subjected to exactly the same treatment as standard cellulose. The sodium hydroxide solutions were carbonate-free and were handled in the manner described in the previous paper (9).

Results

The heats of adsorption of sodium hydroxide, from a solution of a concentration in each case the same as that employed in the mercerizing pre-treatment, were determined with all the mercerized cottons. The results of these determinations, together with the heats of adsorption of sodium hydroxide from solutions of the same concentrations by standard cellulose [see curve for sodium hydroxide in Fig. 1 of previous paper (9)] are given in Table I and Fig. 1. For reasons that will appear later, the difference between the heat of adsorption by the standard and that by the mercerized cotton, at the same alkali concentration, is given in the final column of Table I. This quantity has been named the "heat of mercerization".

The heats of wetting of the various mercerized samples by water and by absolute methyl alcohol were determined. The results are presented in
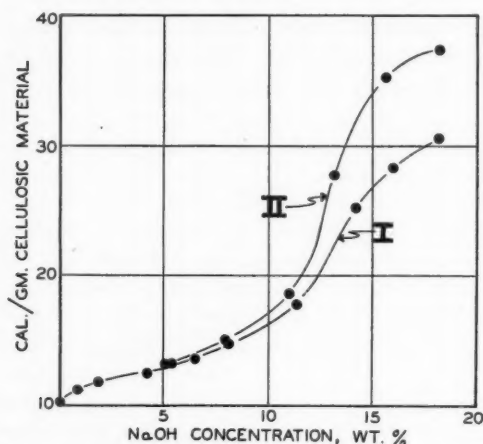
FIG. 1. *Heats of adsorption of sodium hydroxide by standard cotton and by various mercerized cotton samples. I. Standard cotton. II. Mercerized cottons.*

TABLE I

THE HEAT OF ADSORPTION OF SODIUM HYDROXIDE BY MERCERIZED AND STANDARD COTTONS, AND THE HEAT OF MERCERIZATION

.Sodium hydroxide concentration (mercerizing and adsorbing), wt., %	Heat of adsorption of NaOH on standard cotton, cal./gm. cotton	Heat of adsorption of NaOH on mercerized cotton, cal./gm. cotton			Heat of mercerization, cal./gm. cotton
		Individual determinations		Mean	
5.04	12.96	13.24	13.13	13.19	−0.23
8.00	14.41	14.97	15.08	15.02	−0.61
11.00	17.30	18.49	18.55	18.63	−1.33
13.18	22.57	27.59	27.79	27.69	−5.12
15.69	28.80	35.27	35.17	35.22	−6.42
18.14	30.56	37.25	37.13	37.19	−6.63

(Note: the value 18.77 appears centered in the "Individual determinations" area, aligned with the 11.00 row.)

Table II and Fig. 2. In the last column these results are expressed as percentage of the values obtained with standard cotton. The parallel values of this percentage for the two liquids are very interesting. In the case of the 8.00% mercerized sample, the 103 and 107 are within experimental error. The others show a still closer check.

The times to three-quarter values, determined in the same way as in the first paper of this series (8), were found for the heats of wetting of the mercerized cottons listed in Table II by water and absolute methyl alcohol. These are given in Table III and Fig. 3.

Finally, the heats of adsorption of sodium hydroxide from solutions of several concentrations by a sample of cellulose, mercerized in a sodium
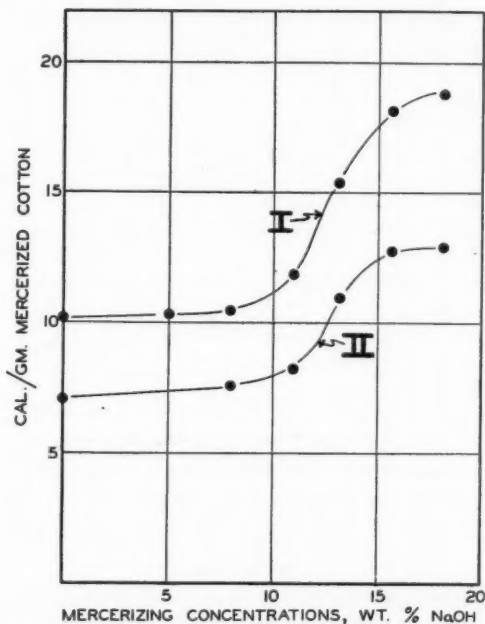
FIG. 2.   *Heats of wetting by water and methyl alcohol of cottons mercerized at several different sodium hydroxide concentrations.   I. Water.   II. Methyl alcohol.*

TABLE II

HEATS OF WETTING OF MERCERIZED COTTONS BY WATER AND METHYL ALCOHOL

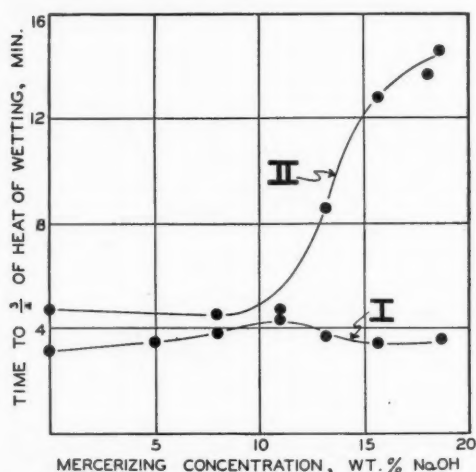| Mercerizing concentration of sodium hydroxide, wt. %	Heat of wetting, cal./gm. cotton Individual determinations		Mean	Per cent of value obtained with standard cotton
Wetting liquid: Water				
0.00			10.18	100
5.04	10.38	10.31	10.34	102
8.00	10.50	10.48	10.49	103
11.00	11.82	11.93	11.87	116
13.18	15.63	15.34	15.48	152
15.69	18.28	18.02	18.15	179
18.14	18.83	18.74	18.79	184
Wetting liquid: Methyl alcohol				
0.00			7.07	100
5.04				
8.00			7.57	107
11.00			8.24	116
13.18	11.03	10.98	11.00	155
15.69			12.78	181
18.14	12.78	12.96	12.87	182

FIG. 3. *Time to three-quarter values for the heats of wetting by (I) water and (II) methyl alcohol of cottons mercerized at several different sodium hydroxide concentrations.*

TABLE III

TIME TO THREE-QUARTER VALUE OF HEATS OF WETTING
OF MERCERIZED COTTONS BY WATER AND
BY ABSOLUTE METHYL ALCOHOL

Mercerizing concentration of sodium hydroxide, wt., %	Time (min.) to three-quarter value of heats of wetting by:	
	Water	Methyl alcohol
0.00	3.2	4.7
5.04	3.5	—
8.00	3.8	4.5
11.00	4.3	4.7
13.18	3.7	8.6
15.69	3.4	12.8
18.14	—	13.7
18.81	3.6	14.6

hydroxide solution of 18% concentration, were measured.   These values are presented in Table IV and Fig. 4.

Discussion

A few scattered determinations of heats of adsorption by mercerized cottons have been reported. Neale (11) made some measurements with sodium hydroxide and a cotton mercerized in 15% sodium hydroxide. He found that at concentrations lower than this the heats were somewhat greater for mercerized than for unmercerized cotton, and he considered this to be due to an increase in the surface of the mercerized form. But at the mer-
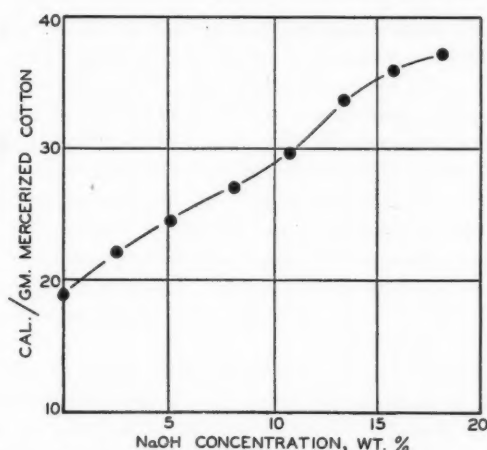
FIG. 4.   *Heats of adsorption of sodium hydroxide on a mercerized (18%) cotton.*

TABLE IV

HEATS OF ADSORPTION OF SODIUM HYDROXIDE BY A MERCERIZED
(18%) COTTON

Concentration of adsorbing NaOH, wt., %	Heats of adsorption, cal./gm. cotton		
	Individual determinations		Mean
2.58			22.08
5.15	24.50	24.50	24.50
8.20	27.05	26.92	26.99
10.85			29.60
13.44			33.65
15.80			35.90
18.14	37.25	37.13	37.19

cerizing concentration his value for heat of adsorption was much the same for both mercerized and unmercerized cottons.   Calculated to the same basis as the present work, these are, for the heats of adsorption of 14.2% sodium hydroxide, respectively 25.9 and 26.2 cal. per gm. of cellulosic material.   The present work gives, for the same concentration, respectively 31.70 and 25.32 cal. (see Fig. 1).   Apparently Neale failed to observe this striking difference between the heats evolved by mercerized and unmercerized cottons when treated with alkali of the mercerizing strength.   The present results are considered to be quite accurate, and one need only refer to Fig. 1 to note the smoothness of the curves and the definiteness of the difference.   So far as is known, this is the first time that this difference has been observed.

Chilikin (5) had determined the heat of wetting of mercerized and unmercerized cottons by water and by a 50% ethyl alcohol solution.   In the abstract of his paper (5), no data were given regarding the concentration employed for

mercerization.   He found that dry cotton liberated 8.14 cal. and dry mercerized cotton, 14.52 cal. per gm., when wetted with water.   These values are low compared with those of Argue and Maass (1) and of the authors. But the increase in the heat of wetting from that of the unmercerized to that of mercerized cottons, namely 78.5%, is comparable (Table II).   His measurements with 50% ethyl alcohol and unmercerized cotton are low compared to the authors' (8).   For unmercerized and mercerized cottons he obtained 8.07 and 13.63 cal., respectively, an increase of 69%.

As far as is known, these are the only references to previous thermal measurements of adsorption on mercerized cottons.   The significance of the differences between the heats evolved when alkali is sorbed on mercerized and on standard cottons will now be considered.

In making the measurements the same final conditions of a certain concentration of alkali in intimate contact with cellulose existed whether one started with a mercerized or standard cotton.   This may be visualized in the following manner.   A measurement of the heat of adsorption of say 10% sodium hydroxide by a sample of dry standard cotton is made.   Subsequently, the sample is removed from the calorimeter, thoroughly washed, dried to the same degree as the original material, and again placed in the calorimeter. The heat of adsorption of the same alkali (10%) by this recovered sample is measured, and the same final conditions probably exist.   But irreversible effects have been eliminated from the second determination.

·The measured heat of adsorption by standard cellulose may be considered as made up of the heat of adsorption of sodium hydroxide, that of water, and the heat involved in irreversible changes such as those in the crystal structure (6) and the formation of any new surface (10, 15).   The latter irreversible changes are called here the "heat of mercerization" (not to be confused with the total heat of adsorption of alkali of mercerizing concentration).   The measured heat of adsorption by mercerized cotton may be considered as made up of the heats of adsorption of sodium hydroxide and of water.   But any heat involved in structural and surface changes has been eliminated.

The difference, which has been tentatively called the "heat of mercerization", is the heat involved in any permanent irreversible changes that occur when cotton cellulose is mercerized.   This quantity is of great interest, and to date has not been measured in this way.   Two points are of particular interest, namely, the endothermicity of the quantity, and the question of what the irreversible changes are.   The latter will be considered first.

For concentrations of alkali lower than 5%, the curves in Fig. 1 coincide. Apparently up to a concentration of 5% the adsorption of sodium hydroxide is wholly reversible.   At concentrations from 5 to 10% some irreversibility takes place, numerically up to one calorie.   Above 10% the difference increases very rapidly until at 15% it is more than 6 cal.   Above 15% the difference does not increase very much.   At 18% it is about 6.6 cal.

These changes parallel very closely the extent to which changes occur both in the crystal structure and in the new surface on mercerization.   When the

concentration is above 10%, the crystal structure begins to change to a new lattice.   This change is irreversible, and is greater with increasing concentration from 10 to 15%.   It is practically complete when the concentration is 15%.   At the same time the available internal surface of the cellulose increases in a like manner, that is, slowly at first then very rapidly, and finally at concentrations greater than 15%, slowly again.

It is therefore considered that the "heat of mercerization" arises from the changes of the crystal structure and the formation of new surface, which properties constitute the essence of mercerization.   The other point of interest, namely, the endothermicity, will now be considered.

Endothermicity

That the "heat of mercerization" should be endothermic seems quite reasonable.   Any change such as the formation of another crystal form and of new surface probably requires energy.   Energy is required for the cellulose to assume the higher "activated" state to which Neale refers (10).   This energy change, if it comes from heat, would give rise to an endothermic effect. The endothermicity of the "heat of mercerization" lends support to the consideration that it is a measure of these structural changes in the mercerization process.

It has often been observed that mercerization proceeds as readily at a lower alkali concentration if the temperature is lowered.   This would appear to refute the observation of the endothermicity of the "heat of mercerization" because an endothermic reaction usually proceeds better with an increase in temperature.   However, though this in itself may be true, another highly exothermic process is occurring at the same time, and this process is much more vital to the mercerization changes.   This is the adsorption of alkali, which, being highly exothermic, would probably proceed much better at lower temperatures.   The relative magnitude of the heats involved in the absorption and mercerization processes is such that the increased adsorption would far outweigh the depressing effect on endothermicity, when the temperature is lowered.

Further support of this interpretation of the heat of mercerization comes from some measurements made in this laboratory of the specific heat of mercerized as compared to unmercerized cotton.   Shipley, Maass, and Campbell (14) found that the mercerized cotton has a higher heat capacity (specific heat).   A higher heat capacity indicates more internal or potential energy, and heat would have to be adsorbed for the cellulose to assume such a condition.   The endothermic "heat of mercerization" is probably the heat so employed.

The increased reactivity of cellulose pretreated with alkali of mercerizing concentration has been observed for a long time.   The effect on the adsorption of water vapour of varying the concentration of the alkali in the pretreatment was studied by Urquhart and Williams (15).   This was virtually the only study reported in which the effect of concentration was closely examined.

Many cases of the increased reactivity towards various reagents have been reported, where cottons usually completely mercerized were employed.

Heats of Wetting

The heats of wetting of the various mercerized cottons by water and by absolute methyl alcohol were found to confirm the varied evidences of increased reactivity. The increase in reactivity when the concentration of mercerizing alkali is increased goes through the same changes found by Urquhart and Williams (15) for water vapour sorption, being very slow up to a concentration of 10%, then very rapid till the reactivity reaches a much higher level at 15%. The greatest amount of water sorption observed was 1.57 relative to that by ordinary untreated cotton. The present investigation indicates as much as 1.84 for the heat evolved relative to that for standard cellulose.

The increase for both water and methyl alcohol is the same, within experimental error, over the whole range of pretreating alkali concentrations. This supports the contention of Neale and of Urquhart and Williams that the change of surface is a capacity, not an intensity, factor. According to this view, the percentage increase of the heats of wetting is a measure of the percentage increase of the same kind of surface as existed in the original untreated cotton.

It is worth while recapitulating. When alkali reacts with cellulose, two phenomena may occur at the same time. A change in the crystal lattice takes place when the alkali concentration exceeds a critical value, and this change is then accompanied by a marked increase in the internal surface of the cellulose, apparently causing the formation of more of the same kind of surface originally in the standard cotton. These changes have been linked up with a so-called "heat of mercerization". But the question of the relationship, that is, how the lattice change influences the adsorption capacity, is far from clear. Probably closely linked with this question is another, namely, how the crystal lattice change itself occurs. At present it is possible only to speculate on these questions.

Campbell (4) has suggested that the crystal lattice change may occur by means of a recrystallization process, the cellulose chains partially dissolving in the alkali, and the new crystal form, being more insoluble, reprecipitating. This would have to occur in such a way that the mercerized material which has been recrystallized would have a new micellar distribution giving an increased surface.

Pockets

Further, Campbell has suggested the existence of pockets or voids in ordinary cotton. This speculation arose from measurements made with water and various liquids on the specific volume of cellulose; also, the anomalous behaviour of alcohol sorption at low vapour pressure supports this idea (13). The speculation could be applied to mercerized material as well, where conditions may favour the formation of more voids. In fact some such idea

may be needed to explain the time to three-quarter values of the heat of wetting of mercerized cottons by water and methyl alcohol.

These values are given in Fig. 3 and Table III. The time value for mercerized cotton wet by water deviates very little from that for a standard cotton. Apparently water is able to wet the newly formed internal structures quite readily. However, in the case of methyl alcohol a large increase is shown in the time to wet the mercerized cottons when the pretreating concentration is above 11% sodium hydroxide. This requires some explanation.

It must be kept in mind that the cotton, after mercerizing treatment, is dried. Bonds between fibrils or micelles, or both, are formed on removal of the water (3), and pockets may be made. On rewetting the internal surfaces, water easily opens up these closed spaces. However, the solvent power of methyl alcohol in regard to these bonds is considered to be less than that of water. Methyl alcohol, therefore, may wet all the available surface less readily, and the structural changes above a mercerizing concentration of 11% are such that the ability of methyl alcohol to wet the surface decreases greatly. Eventually, however, methyl alcohol gives the same relative increase in adsorption heat as does water.

Heats of Adsorption of Sodium Hydroxide

In Table IV and Fig. 4 are given the heats of adsorption of sodium hydroxide of different concentrations by a sample mercerized with 18% sodium hydroxide solution. As Neale has found, the heats of adsorption of alkali below mercerizing concentration are greater than for unmercerized cotton. The curve from 0 to 18.14% alkali approaches a straight line relationship for the heat evolved.

The adsorption of alkali below the mercerizing concentration shows the increased reactivity of mercerized cotton. However, in order to compare this quantitatively with the adsorption of water and methyl alcohol, all irreversible effects must be avoided. The adsorption is reversible up to 5%. Therefore the relative alkali sorption by mercerized cotton, as compared to that of standard cotton, can best be compared at this concentration.

When the sodium hydroxide concentration is 5.15% the heat evolved for mercerized (18%) cotton is 24.50 cal., and for standard cotton, 13.10 cal. The increase in the amount of adsorption, 87%, compares quite favourably with 84% for water and 82% for methyl alcohol. This is further confirmation of the hypothesis of an increase in surface, of which the adsorption quality is constant. The larger value for the alkali is a little beyond experimental error.

The adsorption of alkali is essentially different from that of water or methyl alcohol. The last two have a very similar and relatively simple mechanism of sorption. Alkali sorption, on the other hand, is evidently quite complicated and is a controversial subject. As was elucidated in the previous paper (9), the heats of adsorption changes at lower concentrations up to 5 or 6% were considered to be due to new surface being made available by ordinary swelling.

The same mechanism of swelling probably occurs in the case of mercerized cellulose. Moreover, the looser structure usually associated with the mercerized state may permit even more of this ordinary swelling than for standard cellulose. This could readily account for the discrepancy observed between the relative increases of the heats of adsorption of alkali as compared with those of water and methyl alcohol on mercerized (18%) cotton.

Time Factor

The effect of time of immersion on the degree of change was investigated. A sample of cotton was immersed for 12 hr., as well as 3 hr., in 11.0% sodium hydroxide. The sample immersed for three hours gave a mean heat of adsorption of 18.63 with 11.0% alkali. One value was 18.77 cal. The sample immersed for 12 hr. gave a mean of 18.91 cal., one value of which was 18.82. Apparently the change at this initial concentration is negligible from 3 to 12 hr., i.e., within the experimental error.

Further, a sample of standard cotton was immersed in 18.81% alkali for three minutes, then washed and dried. The heat of wetting with water was found to be 18.88 cal. A sample immersed in 18.14% sodium hydroxide solution for three hours gave 18.79 cal. Also, the heat of adsorption of alkali by the sample immersed for three minutes in 18.81% alkali was 38.0 cal., as compared to 37.82 cal. for the sample immersed for three hours in 18.14% alkali. Apparently, in three minutes at the most, practically all the adsorption and mercerization changes possible can take place.

The rapidity of the action of alkali in mercerization is probably immeasurably large. This would seem to detract from the recrystallization hypothesis of Campbell. It is difficult to conceive that recrystallization and possible accompanying structural changes could occur in such a short time. However, it may be possible to speculate on the parallel between the changes in the crystal lattice and the changes in available surface.

### Physical Structure of Cellulose

The present conception of the cellulose molecule is that it is a chain made up of an indefinite number of glucose anhydride units. The connection between each of these units is a primary valence link through oxygen. The chains are held together in bundles by secondary valence linkages between each chain; and it appears that in this way from 50 to 70 chains are bound together in what is variously called a "micelle" or a "crystallite". Maass and Campbell (7) consider that these bundles are not individual crystallites, rather that the cellulose is a ramifying network of the bundles of chains, which bundles branch off and rejoin in a haphazard manner, and whose only claim to individuality may be in an average width.

Presumably the unsatisfied secondary linkages on the outside of each bundle link the various bundles, to make up the cellulose fibre with which one is familiar. Any wetting or adsorption will occur on the outer surface of the branches or bundles, to satisfy any of the residual secondary valences.

Now, though it does not seem possible at this point to state how the alkali changes the crystal lattice, it is possible to speculate on the parallel between these changes and the formation of new surface. X-rays have shown that the distance between the glucose anhydride units in the primary chains is unaltered by mercerization (6). This spacing may be most important for any material adsorbing on the surface of the branches (or bundles). At the same time, alkali does alter the other lattice dimensions. Thus it affects the arrangement of the chains relative to one another, hence, the cross linkages (secondary valence) between the chains. It is natural to assume that under these new conditions, at equilibrium, the number of chains in a bundle may alter. Apparently this number is reduced so that more surface (of the bundles) is exposed, but surface of essentially the same kind as before alkali treatment, if the primary spacing is the most important for simple adsorption or wetting potentials. If a process of this nature does occur, it would account for the parallel between the lattice change and the surface increase.

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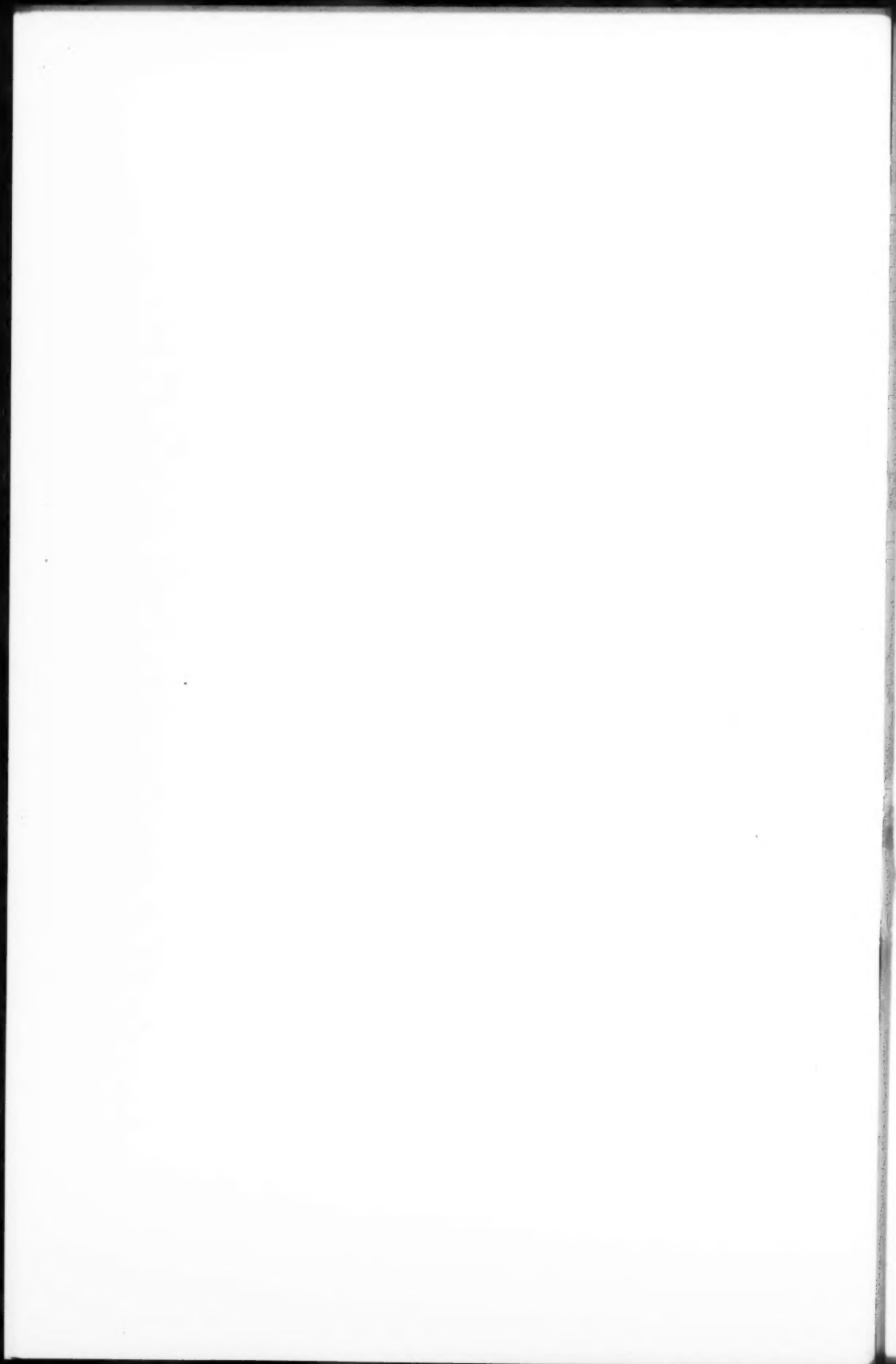
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